

PARTICULATE MATTER (PM_{2.5}) SPECIATION GUIDANCE DOCUMENT

Third DRAFT

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FOREWORD

This document contains information regarding program goals and objectives, and sampling equipment; guidance for sample collection, network design, selection of target analytes, quality assurance, and network operations for the PM_{2.5} speciation program. The guidance provides managers, site operators, laboratory services support personnel, and regulatory compliance data analysts the information needed to implement their PM_{2.5} chemical speciation program. Comments on this, the third draft version, are welcome. Please address comments to:

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1.0 INTRODUCTION

1.1 Purpose

The EPA anticipates that approximately 300¹ monitoring sites will be included in the full chemical speciation network. About 50 NAMS (National Ambient Monitoring Stations) sites will be used for determining long-term trends of selected PM_{2.5} constituents and an additional 250 sites will be used to enhance the trends network and provide State and local agencies information for developing effective State Implementation Plans (SIPs). Approximately 50 of the 250 chemical speciation sites will be integrated with the related Supersites monitoring program which is discussed in Section 1.5.4 of this document. When States and local agencies implement their individual speciation networks, they will be given flexibility by the EPA in terms of selecting sites and sampling technology, sample collection period, site mobility, and identifying additional or alternative target analytes. As States consider integrating a portion of their speciation network with the designated Supersites, they are encouraged to develop partnerships with the academic community and related agencies responsible for specific Supersites studies.

The principal focus of this speciation monitoring guidance document is to provide an overview of the principles and procedures necessary for developing and implementing the chemical speciation network. The guidance is specific and prescriptive for the routine NAMS trends portion of the program, and more conceptual where addressing the additional 250 “State/local” NAMS sites. Much of the material contained in this document dealing with siting and sampling systems, sample and data analysis methodologies, and quality assurance for the NAMS trend sites can be adapted for use in State and local speciation monitoring networks. The intended target audience for this document includes managers, site operators, laboratory services support personnel, and regulatory compliance data analysts involved in PM_{2.5} chemical speciation program implementation. The guidance is organized as follows:

- ▶ **Section 1** gives an overview of the program requirements, goals, objectives, related program efforts and highlights relevant documents and references;

¹ 300 sites are used as an estimate of operational units for planning purposes. The actual number of sites and samplers will be influenced by network design plans submitted by State and Local agencies in relationship to the total resources budgeted for PM_{2.5} chemical speciation.

- ▶ **Section 2** provides a description of data uses - NAAQS support and implementation plan development (trends, control strategies, model validation, source apportionment, and visibility);
- ▶ **Section 3** provides a discussion of particle size distribution, major constituents of PM_{2.5} and potential emission source contributions;
- ▶ **Section 4** provides technical guidance for network design and gives a list of the 54 core NAMS chemical speciation trends sites;
- ▶ **Section 5** discusses sampling artifacts, interferences, limitations and some general difficulties in making ambient aerosol measurements;
- ▶ **Sections 6 and 7** provide a description of the principles, procedures, and equipment used to sample and analyze air sample filter deposits for particle species; and
- ▶ **Sections 8 and 9** provide a discussion of the quality system requirements, data validation, and records management.

1.1.1 Summary of Changes and Revisions

A summary of changes and additions made as part of this revision to the guidance include:

- ▶ A cross-link of PM_{2.5} network elements and program monitoring objectives table is added as Table 1-1.
- ▶ A discussion of the State and local non-routine NAMS (approximately 200 sites) requirements is added as Section 1.2.2.
- ▶ A brief discussion of the Supersite satellite speciation sites (approximately 50 sites) and linkage to the PM_{2.5} speciation program is added in Section 1.5.3.
- ▶ A discussion of the PM_{2.5} speciation Data Quality Objectives developed for the routine NAMS trend network is included in Section 1.7.
- ▶ A significant revision and expansion of the Data Analysis Section 2.0 is incorporated.
- ▶ Changes to the proposed sites for the NAMS trends network as recommended by States, and indication of the proposed co-located sampling sites are made in Table 4-1. A revised map of the proposed sites is also included as Figure 4-1.
- ▶ A section on filter media artifacts is added as Section 5.8.
- ▶ The addition of Table 6-2 has been added, which provides a comparison of the candidate speciation sampling system designs and target analytes analyzed from each filter medium.

- ▶ Schematic diagrams for each candidate sampling system have been included as Figures 6-1 through 6-4.
- ▶ Revision of Figure 7-1, which is a flow diagram of the sample analysis Delivery Order.
- ▶ Significant revision of Section 8.0 on Quality System Requirements for Sampling and Analysis and Section 9.0 on Data Validation and Records Management.

1.2 Background

PM_{2.5} chemical speciation is included in the monitoring requirements and principles set forth by the **Federal Register** (62 FR 38763), promulgated as part of the PM_{2.5} National Ambient Air Quality Standard (NAAQS) review completed in 1997. As a requirement of this rule, a chemical speciation network of trends sites to provide a basic, long-term record of the characterization of the metals, ions, and carbon constituents of PM_{2.5} is. About 50 sites will be used for determination of trends. These sites will be part of the National Air Monitoring Stations (NAMS) network and will provide nationally consistent data for assessment of trends. This network will serve as a model for other chemical speciation efforts and represents a small fraction of the chemical speciation effort that EPA expects to support with Federal funds.

EPA anticipates that approximately 300 sites will comprise the full chemical speciation network. In addition to the 50 NAMS sites for the trends network, another 250 sites will be implemented to enhance the required network and provide information for developing effective State Implementation Plans (SIPs). These sites will be allowed flexibility in terms of sampling frequency, site selection, site mobility, and addition of target species. For example, some areas may choose to focus on specific episodes or seasons, such as a winter time wood smoke problem. Retaining a minimum of 50 core sites with spatial and temporal consistency for long-term trends allows States to use the other 250 sites to address regional and local issues as needed.

At a minimum, the chemical speciation network will quantify mass concentrations and significant PM_{2.5} constituents which include trace elements, sulfate, nitrate, ammonium, and carbon. This series of analytes is very similar to those measured within the Interagency Monitoring of Protected Visual Environments (IMPROVE) program. Technical and practical rationale exist for merging monitoring efforts with IMPROVE. The technical connections between visibility and PM_{2.5} aerosols are given in Section 1.5.5.

The **Federal Register** (62 FR 38763) describes the initiation of a PM_{2.5} chemical speciation network of approximately 50 core NAMS for routine speciation monitoring. About twenty-five of the monitors are to be collocated at the Photochemical Assessment Monitoring Stations (PAMS) component of NAMS, with the remaining sites to be selected in coordination

among EPA, Regional Office Administrators, and the States. EPA recognizes that some PAMS locations may not be prime sites for locating the monitors and will accept alternative monitoring plans with technical justification for alternate locations. Speciation samples will be collected every 3 days at the NAMS sites.

EPA does not believe that a single nationwide approach to speciation sampling and analysis is the best approach for all 300 locations. The EPA expects that most sites will follow a sampling and analysis program similar to the core NAMS sites; however, alternative speciation approaches for non-routine NAMS will be considered on a case-by-case basis through negotiation by State agencies with EPA Regional Offices and Headquarters. EPA encourages State and local agencies to consider additional chemical analyses beyond the constituents specified for NAMS. For example, detailed analysis for compounds comprising the organic carbon fraction could provide valuable insight into development of more refined source-receptor relations, particularly in areas with significant carbon based aerosols. EPA also encourages the use of continuous monitoring techniques to the extent possible. Recent advances in measurement technologies have provided reliable and practical instruments for particle quantification over averaging times of minutes to hours. Commonly used continuous particle monitors measure inertial mass, mobility, electron attenuation, light absorption, and light scattering properties. The EPA has prepared *Guidance for Using Continuous Monitors in PM_{2.5} Monitoring Networks*, (U.S. EPA 1998b) to describe available continuous monitoring methods for suspended particles.

On July 18, 1997, the U.S. EPA promulgated a new NAAQS for particulate matter (PM) in 40 CFR Parts 50, 53, and 58, *Federal Register* (62 FR 38761, 62 FR 38763). The NAAQS applies to the mass concentration of particles with aerodynamic diameters less than 2.5 μm (PM_{2.5}) and 10 μm (PM₁₀). The suite of PM standards is revised to include an annual (long-term) primary PM_{2.5} and a 24-hour (short-term) PM_{2.5} standard. The NAAQS for PM_{2.5} specifies the following:

- ▶ The three-year average of the annual mean of PM_{2.5} concentrations is not to exceed 15 $\mu\text{g}/\text{m}^3$. The average may be based on a single community-oriented monitoring site or the spatial average of community-oriented monitoring sites in a community monitoring zone (CMZ).
- ▶ The 3-year average of the annual 98th percentiles of twenty-four-hour PM_{2.5} concentrations is not to exceed 65 $\mu\text{g}/\text{m}^3$ at any population-oriented monitoring site in a Metropolitan Planning Area (MPA).

The deployment of the national PM_{2.5} monitoring network is a critical component in the implementation of the new NAAQS. Substantial resources are being provided to support the national monitoring network of gravimetric PM_{2.5} sites. This network will comply with the information provided in President Clinton's Directive of July 16, 1997 (62 FR 38421) and regulations provided in the ***Federal Register*** (62 FR 38761, 62 FR 38763). The data from this network will drive an array of regulatory decisions, ranging from designating areas as attainment or nonattainment, to developing and tracking cost-effective control programs.

Data derived from the PM_{2.5} monitoring network include both aerosol mass measurements and chemically-resolved or speciated data. Mass measurements are used principally for identifying areas of attainment or nonattainment. Chemical speciation data serve the needs associated with assessing trends and developing mitigation approaches to reduce ambient aerosol emissions in relation to SIPs. These needs include emission inventory and air quality model evaluation, source attribution analysis, and tracking the success of emission control programs. These chemical measurements will also provide data to support regional haze assessments, which is also a primary objective of IMPROVE.

The overall data gathering needs for the PM_{2.5} program are being addressed by the following objectives and schedules:

- ▶ Designation of Federal Reference or Equivalent Method (FRM/FEM) samplers to collect data for PM_{2.5} NAAQS comparison purposes.
- ▶ Establishment of a PM_{2.5} gravimetric and continuous monitoring network by December 31, 1999.
- ▶ Collection, measurement, and storage of quality-assured mass data beginning on January 1, 1999, to support NAAQS comparisons and regional haze assessments.
- ▶ Development of a national chemical speciation sampling and analysis program by October 1999.

1.3 Programmatic Requirements

The full chemical speciation program incorporates a balance of prescribed requirements, particularly for the routine NAMS, and the allowance for alternative sampling and analysis protocols for other sites within the program. It is not possible to anticipate the full range of sampling and analysis approaches State and local agencies may consider, especially in light of

emerging technologies and forthcoming aerosol characterizations across different locations. In addition to providing specific guidance for routine NAMS, this document largely provides support or background information that can be utilized in formulating sampling and analysis plans for non-routine NAMS. A description of required sampling and analysis plan elements and procedures for submitting monitoring network descriptions for EPA approval is provided in Section 1.5.2.1.

State and local agencies should submit preliminary speciation sampling and analysis plans as part of all network description submissions to the appropriate Regional Offices. The due date for final network descriptions was July 1, 1998. Recognizing that little lead time exists between availability of guidance and the implementation dates, EPA expects final submission of the speciation network design plans by July 1, 1999. Furthermore, subsequent annual updates are required to be submitted by States as part of their annual State monitoring report due July 1, or an alternative date negotiated by the State and the EPA Regional Administrator, per the *Federal Register* (62 FR 38763).

1.4 Program Goals and Objectives

The overall goal of the PM_{2.5} monitoring program is to provide ambient data that support the Nation's air quality program objectives. The entire PM_{2.5} monitoring program includes a substantial mass network in addition to the subject speciation program. While the elements of this large program may be administered through individual mechanisms as shown in Table 1-1, all elements must complement one another in meeting multiple objectives as an overall integrated program. These overarching objectives are presented as context to a more detailed discussion of specific objectives addressed through the speciation program.

In prioritized order, the major programmatic objectives for the routine NAMS PM_{2.5} chemical speciation include:

- ▶ annual and seasonal spatial characterizations of aerosols;
- ▶ air quality trends analysis and tracking progress of control programs; and
- ▶ development of emission control strategies.

Objective 1. Annual and Seasonal Spatial Characterizations of Aerosols

The analytes chosen, specific sampling periods and frequency, spatial resolution, and data accuracy affect the overall data use. The primary use of these data will be to develop general characterizations of aerosols across the major urban areas of the country, depicting seasonal and annual patterns. To the extent that networks include sites located in "transport" and/or

“background” locations, similar characterizations of rural/regional environments, especially in combination with the IMPROVE program, are expected outputs. This objective serves an important need to gain understanding of the characterization of the aerosol nationwide. The following objectives all require this initial characterization step, which in practice translates into developing common spatial and seasonal/annual displays of aerosol components. Accordingly, this objective is the highest priority. An analysis of the speciation data may lead to the classification of air sheds into groups with similar particulate composition and concentration.

Table 1-1. Cross-link of Network Elements and Monitoring Objectives

Network Element	PM _{2.5} Monitoring Objectives						
	NAAQS Comparisons	Public Information /PSI	SIP Development (AQSM, EI, S-R)	Assess SIPs Trends	Health/ Exposure	Visibility Assess	Methods Testing
FRM Mass (110 sites)	✓			✓	✓		
Continuous Mass (125 sites)		✓	✓		✓		
Speciation (50 NAMS Trends sites)			✓	✓	✓	✓	
Speciation (250 State sites)			✓		✓		✓
Speciation (100 IMPROVE sites)			✓	✓		✓	
Supersites (5-8 sites)			✓		✓		✓

This would allow the results of intensive studies to be more broadly applied to appropriate locations and reduce excessive redundancy of efforts on a national level.

Objective 2. Air Quality Trends Analysis and Tracking Progress of Control Programs

The use of observational data to play a central role in ongoing SIP improvement has been encouraged by the scientific community through the 1991 National Academy of Sciences Report on Tropospheric Ozone (NRC, 1991) and the forthcoming North American Research Strategy for Tropospheric Ozone (NARSTO) Assessment (Planned for release in 1999). The ability to detect trends in ambient concentrations that are associated with planned air quality control efforts must be incorporated in SIP assessments.

Objective 3. Developing Emission Control Strategies

A combination of prospective air quality modeling and semi- quantitative source attribution analyses will generate objective information for decision makers with underlying emission control decisions. Speciated data will be used in evaluating air quality model performance and fulfilling the requisite emission fields. A variety of source attribution techniques will be exercised. Recognizing the uncertainties and limitations in models, inventories, and sampling/analysis methods, this objective is of lower priority.

There exists a constant need to develop information that may lead to more definitive associations between adverse health impacts and specific aerosol properties. The speciation program provides greater chemical resolution than standard mass measurements and therefore, should provide data of value to health studies. Nevertheless, this routine speciation program must enlist input from health scientists to optimize overall value. For example, emissions from combustion processes include fine particles containing trace elements of varying toxicity. Information is needed which relate emissions characteristics from processes such as fossil fuel combustion, prescribed burning, and wild land fires, to urban and nonurban PM_{2.5} concentrations and the magnitude of toxicity relative to the exposure of populations to such particles. In contrast, some PM_{2.5} may not be harmful, such as the PM_{2.5} transported from North Africa, which is thought to primarily be very finely ground limestone or calcium carbonate.

1.5 Program Components

The speciation program includes multiple elements with different, yet overlapping objectives. The major program components include:

- ▶ The 50 or so NAMS dedicated to characterizing major aerosol mass components in major urban areas of the United States for discerning long-term trends and providing an accountability mechanism to assess the effectiveness of emission mitigation programs;
- ▶ Approximately 200 dedicated State/local sites for evaluating source-receptor relationships in support SIPs; including more detailed characterizations, data for source attribution tools and evaluation of air quality simulation models and emissions inventories;
- ▶ Approximately 50 sites to be integrated as “satellites” to the Supersites program (see below);

- ▶ Between 5 to 8 Supersites areas identified to serve as scientific research platforms for addressing advanced monitoring technology assessments, investigating atmospheric processes and their impacts on public health and epidemiological issues; and
- ▶ Approximately 100 IMPROVE sites dedicated to assessing regional haze progress.

1.5.1 National Air Monitoring Stations (NAMS) Trend Sites

The Code of Federal Regulations (CFR), Part 58 contains the EPA ambient air quality surveillance regulations. Section 58.20 of 40 CFR, Part 58 requires States to provide for establishment of air quality surveillance systems as part of their State Implementation Plans (SIPs). The air quality surveillance system consists of a network of monitoring stations designated as State and local Air Monitoring Stations (SLAMS), which measure ambient concentrations of those pollutants for which standards have been established in 40 CFR Part 50. NAMS, which are a subset of SLAMS, and PAMS (Photochemical Assessment Monitoring Stations) must also meet the requirements of 40 CFR Part 58, Appendices A (Quality Assurance Requirements), C (Ambient Air Quality Monitoring Methodology), D (Network Design Criteria) and E (Probe and Path Siting Criteria).

The NAMS sites are dedicated to providing air quality trends over time and therefore, require consistent sampling and analysis protocols. The EPA expects that sites not designated as NAMS may conform to similar protocols. Recognizing that a national protocol for trends does not meet the specific needs for every location, the EPA will allow deviations from NAMS protocols at non-routine NAMS sites when adequate network descriptions and justification are provided in the plans described below (Section 1.5.2.1). The major requirements for each NAMS network description include:

- ▶ **Sampler type** - To ensure consistency, the EPA, through consultation with the speciation workgroup, will determine the sampler type(s) utilized at NAMS. The sampler will be a multiple filter device capable of collecting the target analytes listed below.
- ▶ **Sampling Frequency** - One 24-hour sample will be collected at each site every 3 days. As a result of feedback obtained from the NAS, EPA is planning to increase the sampling frequency to once per day at 10 core NAMS sites in year 2000.
- ▶ **Target Analytes** - Elements will be determined using X-ray fluorescence spectroscopy (XRF); major ions [sodium, potassium, sulfate, nitrate, ammonium] will be determined

using ion chromatography (IC); and total, elemental, organic and carbonate carbon will be determined by thermal optical analysis (TOA).

1.5.2 State/Local sites

A substantial portion of the program lacks the prescriptive natural design elements associated with the NAMS to accommodate area specific tailoring of measurement programs, recognizing both the diverse character of aerosols across the United States and the benefit of regional and local knowledge and expertise. This element of the speciation program is the most flexible component of the entire PM_{2.5} monitoring program. In broad terms, the principal objective of this program is to support the development of emission control strategies. Tasks associated with strategy development that require speciated data include airshed characterization (i.e., resolving aerosols into its spatial, temporal, chemical and size properties), operation of source attribution tools (e.g., CMB8, UNMIX), an array of observational analyses that help to understand transport phenomena and precursor limiting identification (e.g., ammonia versus nitrogen oxides), and evaluation of air quality stimulation models and its associated emissions input fields. This emphasis on SIP development is not intended to preclude other important objectives such as long term trends or ongoing assessment of strategy effectiveness. Indeed, in many cases State and local agencies may determine that available NAMS need very similar complementary sites given the spatial complexity posed by aerosols combined with a relatively limited 50 site national network. Nevertheless, the State and local sites need to address the near term development of control strategies when viewed more broadly across a matrix of principal objectives by program elements.

A measurement approach at the State/local sites that deviates from the NAMS is reasonable, given that the objectives for these sites are not identical to NAMS objectives. Therefore the overriding guidance for State and local agencies is to establish network-specific objectives which will drive the design of their sampling and analysis program. Any program proposed is required to meet the requirements described below in Section 1.5.2.1. Examples of measurement approaches that might be pursued by State and local agencies include:

- ▶ ***Increased temporal resolution of major components*** to support tools and studies that benefit from resolution greater than that typically provided by 24 hour filter-based samples in the NAMS; example needs include: elucidation of diurnal emissions profiles, evaluation of air quality simulation models, drive source attribution methods and support health effects and exposure studies. This increased time resolution could be accomplished through some combination of filter based methods which provide sample material for detailed laboratory analysis and emerging continuous techniques that provide high time

resolution capability (e.g., 4 hour sampling period) with potentially limited labor requirements.

- ▶ **Organic chemistry speciation** to provide detailed information of the major fractions of total carbon particulate content. Detailed organic chemistry speciation is extremely useful for source apportionment techniques that relate emission source “markers” to ambient data, and by extension might provide important accountability markers for emissions control programs, and potentially provide support for a range of health effects and exposure studies.
- **Exploratory “movable” sites** to provide analyses for emissions strategy development. The NAMS are designed as fixed site platforms to provide consistent measurements over time. This approach is not necessarily optimized for objectives that attempt to characterize a spatially heterogeneous airshed as an initial basis for emissions strategy development. Therefore, consideration could be given to moving speciation samplers (filter based or continuous) across different platforms at sampling intervals that enable a collection of characterizations at several locations. Examples might include rotation across sites on a biweekly basis up to an annual basis depending on the specific objectives set forth. Flexibility to accommodate movable sampling schemes would open up collaborative possibilities with research organizations investigating health effects and exposure relationships among ambient concentrations and specific communities.

1.5.2.1 State and Local agency monitoring network descriptions and plan elements

The monitoring network descriptions should provide the speciation monitoring strategy and document any deviations from approaches used in the NAMS. Additional guidance is provided in the *Guidance for Network Design and Optimum Site Exposure for PM_{2.5} and PM₁₀* (U.S.EPA, 1997c). At a minimum, the following elements must be included and be reviewed each year as part of the annual network review.

- ▶ **Program Objectives** - A description of the basic technical objectives to be addressed. These objectives should go beyond very generic categories such as “develop control strategies” and address the specific technical needs/issues relevant to a particular area.
- ▶ **Sampling Network Design** - Location and description of sampling platforms, including additional collocated instrumentation as applicable.

- ▶ **Sampler Type** - Plans should provide the vendor name and instrument model selected. Preliminary plans may have to reflect generic descriptions of sampler types.
- ▶ **Sampling Frequency** - In many cases, sampling will be conducted with 24-hour sampling periods on an every 3-day or 6-day basis with exceptions for episodic coverage. These sampling schedules may be analyte or instrument dependent (e.g., use of continuous analyzers).
- ▶ **Target Analytes** - A description of the components to be analyzed, including associated sampling frequencies if analyte specific.
- ▶ **Sample Handling** - A description of the sample collection, transport, laboratory identification and archive procedures. Provide a detailed description (life history) of the sequence of filter collection, transport to analysis laboratory, and subsequent storage for future analysis.
- ▶ **Data Analysis** - This description should include initial data assessments at the sample level; spatial and temporal aggregation techniques; and more refined and exploratory analyses addressing stated program objectives.
- ▶ **Supersites Communications** - A description of mechanisms for interaction with Supersites activities, where applicable.
- ▶ **Program accountability** - A description of the program organizational structure which defines the persons responsible for management, implementation, and quality assurance of the network. Describe the management plan and accountability measures used.

1.5.3 Supersites

In addition to the “routine” chemical speciation network of NAMS trends sites and additional 250 sites for SIP development, the EPA anticipates that special study activities will enhance the information base for control strategy development (emission inventory and air quality model evaluation) and health related studies. As part of this initiative, EPA anticipates establishment and operation of the “Super Sites” network to provide resolved characterizations (time, space, composition) of aerosols as well as related precursor, intermediate, and sink species that lead to greater understanding of PM_{2.5} (and ozone) formation and loss processes. These studies should not be confused with the PM_{2.5} chemical speciation network and are intended to foster collaborative relationships among State/local agencies, academia and industry. The

mechanisms for conducting these projects may include any combination of public/private partnerships, State/local partnerships with EPA, or partnerships with universities. Certain projects may consist of a series of special field studies aimed at supporting ongoing epidemiological studies, and others may be specific to a single area. Depending upon the study location, the EPA may be able to expand upon existing contractual and grant agreements as vehicles for this work. More information on this program is available in the document entitled: *Atmospheric Observations: Helping Build the Scientific Basis for Decisions Related to Airborne Particulate Matter*, (Albritton and Greenbaum, 1998).

1.5.4 Supersite Satellite Sites

The Supersites program and the speciation program operated by State and local agencies must be integrated as each provide valuable complements to one another. Among other objectives, the Supersites provide a means for testing new sampling technologies that eventually may be incorporated into the speciation network. The speciation network provides a needed spatial complement to Supersite areas that may focus on intensive measurement at a very limited number of locations. The EPA believes that the entire speciation program conceptually should be fully integrated with the Supersites program. Practical considerations and area specific needs of State and local agencies logically suggest various levels of coordination, ranging from a less resource demanding information and status communications approach for the 200 sites discussed in Section 1.5.2 to more explicit coordination for 50² satellite sites. The EPA is requesting that State and local agencies join in collaborative partnerships with the appropriate local oversight group responsible for Supersites activities. As of November, 1998, EPA has identified Atlanta, Georgia and Fresno/Bakersfield, California as the initial Supersite locations³. The level of interaction between State/local agencies and Supersite activities is subject to arrangements made by the relevant organizations. Chemical speciation plans submitted by State and local agencies that include a Supersite must address the communication and coordination mechanisms for liaisons across regulatory and Supersites groups. EPA expects that the *minimum* level of interaction would involve the sharing, review of and comment on relevant sampling and analysis

²Counted within the 50 satellite sites are the 10 daily sampling trends sites that are earmarked for long term health panel studies.

³ Supersite contacts for Fresno/Bakersfield include Dr. Marc Pitchford, U.S EPA (702-895-0432) and Karen Magliano (916-322-5350), California Air Resources Board; Atlanta (Dr. Ellis Cowling, North Carolina State University, 919-515-7564 and Dr. Paul Solomon, U.S. EPA, 919-541-2698).

plans with agreement reached between State/local agencies and relevant Supersites organization on the utilization of resources explicitly dedicated⁴ to Supersites integration.

⁴ EPA grant guidance to States on the use of section 103 federal Grants will explain resource allocations set aside for integration with Supersites.

1.5.5 IMPROVE

The 40 CFR 51 Regional Haze Regulation, proposed in the *Federal Register* (62 FR 41137), includes visibility monitoring requirements. The technical connections between visibility and fine aerosols are solid and logically point to a comprehensive monitoring program that services both PM_{2.5} and visibility assessments. The technical connections between the chemical speciation program and visibility monitoring are given below:

- ▶ Fine particles are responsible for nearly all visibility degradation.
- ▶ Visibility extinction budgets are calculated through speciated aerosol measurements; the measurement and analysis approaches are virtually the same for the PM_{2.5} speciation program and IMPROVE.
- ▶ Spatial scales associated with visibility measurements (regional) are frequently the same as spatial scales associated with background and transport PM_{2.5} measurements (regional, urban). It is important to consider including data collected under the Regional Haze program as part of the PM_{2.5} data analysis activities.
- ▶ Sources that affect visibility are the same sources that affect PM_{2.5}, and control programs that influence visibility also influence PM_{2.5} levels.

Clearly, the technical justification exists for merging these monitoring efforts. Similarly, there is value to combining resource planning and network deployment efforts simultaneously as combined planning is far less burdensome than separate efforts. The IMPROVE chemically speciated data will also be useful to the overall PM_{2.5} program. In fact, the nation is currently in the unusual position where aerosols are better characterized in rural/remote environments relative to urban and populated areas due to the effectiveness of the IMPROVE program.

1.6 Data Use and Analysis

The expectations for data emerging from the routine NAMS program should be put in context. In communicating the need for gaining a gross understanding of aerosol concentration, composition, and distribution across the United States, the inherent limitations of such a program are not obvious. As one proceeds down the list of priorities, important limitations arise. For example, the lack of time resolved measurements constrains the ability to interpret air monitoring data with air quality models and emission estimates, both of which incorporate strong diurnal trends. Clearly, the effectiveness of assessment tools increases with more resolved information

(space, time, composition, size, phase, etc.). The aggregate approach (24-hour sampling, 1 size fraction, 1 vertical plane) across all aerosol properties is an acknowledged current shortcoming. This program must reflect a reasonable balance that considers available resources, technological limitations, and other efforts. The EPA recognizes that, in future years, there may be a need to adjust the objectives and requirements for speciation sampling and analysis. Just as control programs need to be assessed periodically, a major data acquisition program should undergo periodic assessments as well. However, there must be careful balance between having a flexible monitoring network which is able to adjust to new technologies as they arise, and the problematic issue of wide scale implementation of innovative technologies with little cohesion between data gathering activities.

Guidance on how to organize and analyze the data is given in Section 2.0. Software applications are needed to easily organize and display the data in meaningful ways which might be of great use in identifying and understanding significant PM_{2.5} characteristics and trends. Personnel resources will need to be identified in order to properly analyze the data.

Within the current network design framework, data collected every third day within the NAMS sites will have limited use for epidemiological studies. A majority of the sites would have to be located in highly populated areas with greater than 500,000 inhabitants, which are more appropriate for health assessment studies. For the longer term, when continuous methods that provide equivalent data become available, the network can be upgraded. As these methods are implemented, they will also provide valuable diurnal information while reducing sampling and analysis costs.

1.7 PM_{2.5} Speciation Data Quality Objectives

An important concern in the collection and evaluation of ambient air monitoring data is the level of uncertainty. Uncertainty arises due to temporal and spatial variability in the ambient air, variability in the samplers, and variability in the laboratory analyses. The data quality objective (DQO) process, a strategic planning approach, is used to structure the PM_{2.5} speciation data collection activity. The DQO process provides a systematic procedure for defining the criteria that the PM_{2.5} speciation data collection design should satisfy, including when to collect samples, where to collect samples, how many samples to collect, and the tolerable level of decision errors. By using the DQO process, EPA assures that the type, quantity, and quality of the data are appropriate for the intended application, while guarding against committing resources to data collection efforts that do not support the program objectives.

For the PM_{2.5} speciation monitoring network, the DQO process will proceed down two tracks due to differing primary objectives. For the NAMS sites, the primary objective is to determine trends on the national level. For the remaining 250 sites, objectives may vary, depending on the regional and/or local data needs. For example, a State with high concentrations of PM_{2.5} might consider the primary objective to be the characterization of the fine particulate aerosol to assist with the development of control strategies, whereas a State with Class I areas might consider the primary objective to be measuring trends in visibility. For each objective, the DQO process might result in different optimal monitoring designs and tolerable errors; therefore, DQOs will be developed with both objectives in mind.

The Monitoring and Quality Assurance Group (MQAG) within the Emissions, Monitoring, and Analysis Division (EMAD) of the OAQPS has initiated an effort to ensure that the data collected by the ambient PM_{2.5} speciation network is of a sufficient quantity and quality to support the intended uses of the data. This effort includes development of DQOs for the NAMS sites dedicated to measuring national trends in the PM_{2.5} species (U.S. EPA, 1998c) and a blueprint of the DQO process for the remaining 250 sites (expected to be available May 1999). A speciation DQO Work Group was developed, and a discussion of the DQOs developed for the trends sites is presented below.

Generally, the DQO process is used to determine the sampling frequency, location of the samples, and tolerable measurement errors needed to achieve desired levels of errors associated with decisions that will be based on data collected by the PM_{2.5} speciation trends sites. Most of the monitoring characteristics have already been established for the trends network as the result of regulations or recommendations from the PM_{2.5} Speciation Expert Panel (Koutrakis, 1998) and PM_{2.5} Speciation Workgroup. Thus, the issues to be addressed with this DQO process included (1) estimating the decision errors resulting from the characteristics of the network, (2) recommending changes to the sampling plan if the resultant decision errors were unacceptably large, and (3) prescribing required measurement precision.

The following items summarize the monitoring characteristics that had been established for the trends network prior to the beginning of the DQO process.

Number of sites: The PM_{2.5} speciation trends network is to consist of approximately 54 sites as proposed by the EPA.

Location of sites: Approximately 25 of the sites are to be located in PAMS areas. The remaining sites are to be selected in coordination among the EPA, Regional Offices, and the States and local agencies. Twenty-four of the 54 proposed sites are in PAMS areas.

The rationale for the selection and the resulting locations of all the sites are documented in Section 4.0.

Sampling frequency: The PM_{2.5} Speciation Expert Panel and EPA have determined that the sampling frequency for the trends sites should be once every 3 days which is documented in *Summary of the Recommendations of the Expert Panel on the EPA PM_{2.5} Speciation Guidance Document* (Koutrakis, 1998).

Sampler type: The sampler will be a multiple filter device that collects 24-hour integrated samples.

Analytes to be measured and the method of measurement: The species to be measured include:

- elements Al through Pb using X-ray fluorescence spectroscopy (XRF),
- major ions (sulfate, nitrate, ammonium, sodium and potassium) using ion chromatography (IC), and
- total, elemental, organic and carbonate carbon using thermal optical analysis (TOA).

The DQO process incorporates input from a planning team consisting of program staff, technical experts, managers, a quality assurance/quality control advisor, and a statistician. This enables data users and relevant technical experts to specify their particular needs prior to data collection. These decision makers decided that the primary objective of the trends component of the PM_{2.5} speciation network is to detect trends in individual component species on a site-by-site basis. Specifically, the decision makers wanted to be able to detect a 3-5% annual trend (increasing or decreasing) with 3-5 years of data.

Although the data collected by the PM_{2.5} speciation network will be invaluable for a multitude of data analyses, the detection of trends is the primary objective of the NAMS portion of the PM_{2.5} speciation network. The decision makers and the PM_{2.5} Speciation Expert Panel concurred with this primary objective and therefore is the one on which the DQOs were based. This means that the tolerable decision errors will be based exclusively on trends analyses, even though other data uses might have larger resultant decision errors. The need for accurate trends at the site level is due to the manner in which the trends will be used. The decision makers decided that trends are needed to evaluate the long-term effectiveness of control strategies. Incorrect estimation of trends may lead to incorrect assessments about the effectiveness of implemented control strategies. Since control strategies likely will be developed, applied, and/or evaluated at the Metropolitan Statistical Area (MSA) level and given that at most one trend site

will be within an MSA, the trends need to be accurate on a site by site basis. Additionally, the decision makers thought that regional or national trends would be difficult, if not impossible, to interpret because of the geographical variability in meteorology, species composition, and control strategies.

Variation in meteorology can mask or attenuate trends that are due to changes in emissions. Given the intended use of the trends data, the decision makers decided that meteorological variation needs to be removed before the trend analysis is performed. That is, the trends in which the decision makers wanted to have the specified decision errors are ones for which the impact due to variation in meteorology has been removed. The details for how this adjustment was accomplished are included in the appendix. Basically, a seasonal component based on the number of days into a year was added to the statistical model of the data.

Lastly, the development of the DQOs was done for four analytes, those being sulfate, nitrate, total carbon, and calcium. The target analytes of interest for the speciation trends sites were selected to include those which have been historically measured within the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. To ensure that data from the speciation trends sites could be compared with IMPROVE data sets, the trends DQO development considered an analysis of the ability to sample and measure selected analytes which are thought to be major components of aerosols collected in both networks (sulfate, nitrate, and total carbon) and whose concentrations could be expected to vary with the implementation and effectiveness of emissions controls. Sulfate is a direct indicator of anthropogenic emissions, primarily from fossil-fuel fired combustion sources and can be effectively measured by most fine particulate sampling systems. Sulfate levels are usually the highest in the eastern United States. In contrast, nitrate is an indicator of secondary atmospheric aerosol formation resulting from nitrogen oxides emissions and is somewhat difficult to quantitatively sample because of volatilization artifacts which can occur in many sampling systems. Nitrate levels are usually the highest in the western United States. Total carbon in fine aerosol particles is associated with wood combustion and mobile source emissions and also represents an analyte which has the potential for either positive or negative sampling artifacts. Calcium was included since it is an element which is generally associated with non-anthropogenic emissions such as windblown soils, mineral materials, and dusts. Calcium is usually assumed to occur in particles predominantly greater than 2.5 microns. Therefore, fine particulate calcium should be present at low background levels and represents an aerosol constituent which is not expected to vary significantly with source emissions controls implementation.

Data from the IMPROVE program was used to estimate the variability likely to be observed in national PM_{2.5} speciation measurements. This was done because each of the analytes

to be monitored at the routine NAMS sites is currently being monitored in the IMPROVE program and the analytical methods used in the IMPROVE program are similar to those to be used in the national program.

The national chemical analysis methods for calcium and total carbon differ from those used in the IMPROVE network. The IMPROVE network uses proton induced X-ray emission (PIXE) to analyze the PTFE filter for calcium and thermal optical reflectance (TOR) to analyze the quartz filter for total carbon. Due to the lack of long-term data collected using EDXRF and TOA, it is an assumption of this DQO process that EDXRF and PIXE have similar percentages of non-detects and levels of precision and similarly that TOR and TOA have similar percentages of non-detects and levels of precision. This assumption is questionable for calcium based on a recent article that indicates that the detection limit for calcium using XRF may be 5 times that for PIXE, 2.4 ng/m³ for XRF versus 0.5 ng/m³ for PIXE (Nejedly, 1998). The recent literature supports the assumption regarding the comparability of TOR and TOA (Birch, 1998).

An additional difficulty in using the IMPROVE data for the national trend network planning is that the IMPROVE sites, by design, are predominantly located in rural areas. This will not be true of the NAMS sites. Anticipated differences in variability of speciated PM_{2.5} data between rural and urban sites was factored into estimates obtained based on the IMPROVE data. This was accomplished by analyzing the data from the urban IMPROVE site located in Washington DC, the only long-term urban IMPROVE site.

Descriptive statistics were calculated and models fitted to assess seasonal trends, time trends, auto-correlation, and variability of sulfate, nitrate, calcium, and total carbon measurements in the IMPROVE data on a site by site basis. The methods and models used to describe the IMPROVE data are documented in the *Data Quality Objectives for Detection of National Trends in Speciated Data* (U.S. EPA, 1998c). Table 1-2 presents statistics on the geometric mean concentrations, measurement error rates, and percentages of non-detects. The measurement error rates and percentage of non-detects are quantities provided from the IMPROVE database. Generally, small non-detect percentages were observed for each of the species across the network. This suggests that the ability of laboratories to detect concentrations of each of the species at levels actually present in rural areas is good. Since urban concentrations are anticipated to be higher than rural concentrations, inability to detect species should not be an issue. Note that the measurement error is small compared to the variability remaining after fitting the model. This can be seen by comparing the coefficient of variation in the second part of the table (measurement error) with the coefficient of variation in the first part of the table (variability remaining after fitting the model).

The decision makers (PM_{2.5} speciation DQO Work Group) agreed that the objective of a 3-5% trend per year needs to be detected with 0.8 power within 3-5 years of initiation of sampling. Table 1-3 summarizes the percent reductions (or increases) that can be detected with 0.8 power under a variety of assumptions. Based on this information it was concluded that even with 1 in 3 day sampling, five years of data will only detect 5% reductions (or increases) in some pollutants. *Daily sampling provides little advantage in trend detection over one in three day sampling relative to the increased cost.* Analyses indicated that power is relatively robust to

Table 1-2
IMPROVE Data Summary

Parameter	Concentration (µg/m ³)		Measurement Error (Average coefficient of variation)		Percentage Non-Detects (%)	
	Mean	Range	Mean	Range	Mean	Range
Sulfate	1.357	0.246-4.932	0.055	0.036-0.124	0.293	0.000-3.343
Nitrate	0.261	0.029-1.321	0.133	0.046-0.502	4.118	0.000-37.021
Calcium	0.026	0.008-0.083	0.089	0.062-0.129	2.078	0.000-13.566
Total Carbon	1.295	0.342-4.119	0.176	0.064-0.421	0.000	0.000-0.000

changes in measurement error up to 2 times IMPROVE's rate. This is because measurement error is small compared to variability left unexplained by the seasonal and time trend component model. Analyses depicting the effect of measurement error if a better data model were developed were evaluated. However, it is anticipated that measurement error may be more critical for uses of the speciated PM_{2.5} data other than trend detection. Therefore, it is advantageous to control measurement error at levels comparable to the IMPROVE data given in Table 1-2. Thus, one in three day sampling for five years with measurement error rates similar to IMPROVE's is recommended for trend identification.

Table 1-3
Increase or Reduction in Power for Two Sampling Periods and Three Sampling Frequencies

Species	Daily Sampling		One in Three Day Sampling		One in Six Day Sampling	
	Three Years	Five Years	Three Years	Five Years	Three Years	Five Years
Sulfate	7.5	3.6	8.6	4.1	10.9	5.2
Nitrate	12.2	5.9	13.0	6.3	15.3	7.4
Calcium	7.4	3.5	8.5	4.1	10.9	5.2
Total Carbon	5.5	2.6	7.3	3.4	10.0	4.8

1.8 Related Documents and References

An expert panel met on May 12-13, 1998, in Seattle, WA, to review an earlier draft of the EPA guidance document for chemical speciation which was also provided for public review and comment through the Internet at the EPA Air Monitoring Technical Information Center (AMTIC) PM_{2.5} bulletin board. The panel represented nationally-recognized expertise in fine particle and aerosol sampling and analysis as well as linkage to the assessment of the role of aerosol chemical components to health effects research. Other participants in this meeting included the EPA Speciation Workgroup and representatives from several States.

The panel reviewed EPA's monitoring strategy, selection of target analytes, samplers, and analysis methods. A summary of the panels findings and recommendations can be found on the AMTIC bulletin board. Specific recommendations, such conducting a speciation sampler intercomparison study, have been addressed and are discussed in this current version of the guidance document.

The *Guideline on Speciated Particulate Monitoring* prepared for EPA by the Desert Research Institute is forthcoming and will be included as an addendum to this guidance document when available. It includes a detailed discussion on the physics and chemistry of atmospheric particles, particulate samplers, laboratory analysis methods, and measurement artifacts and interferences. Other documents are listed below and in the references given at the end of this document.

Guidance for Network Design and Optimum Site Exposure for PM_{2.5} and PM₁₀ (U.S. EPA, 1997a).

Quality Assurance Guidance Document 2.12: Monitoring PM_{2.5} in Ambient Air Using Designated Reference or Class I Equivalent Methods (U.S. EPA, 1998a).

Guidance for Using Continuous Monitors in PM_{2.5} Monitoring Networks (U.S. EPA, 1998b).

Visibility Monitoring Guidance Document, Draft (U.S. EPA, 1998d).

Air Quality Criteria for Particulate Matter (U.S. EPA, 1996a)

EPA Air Monitoring Technical Information Center (AMTIC) PM_{2.5} bulletin board is also accessible via the Internet at: <http://www.epa.gov/ttn/amtic/amticpm.html>

2.0 DATA ANALYSIS

The PM_{2.5} program objectives described in Section 1 will be supported through various data analysis and interpretation activities. In recent years, increasingly greater reliance has been placed on observational data for air quality planning needs beyond NAAQS comparisons; this is especially true of the type of data that will be produced in the PM_{2.5} speciation networks. Many of the recommendations from the NAS Report on Tropospheric Ozone (NRC, 1991) reflect the need to better integrate observations into air quality planning rather than rely completely on emissions-based air quality modeling approaches. That message is being reinforced in the current ozone science assessment conducted through NARSTO; their report is scheduled to be released early in 1999. A new approach for integrating observations in air quality planning through continuous iterative assessments which revisit program objectives and adjust, where practical, the implementation strategies is described in U.S. EPA, 1995a. Observations represent our best attempt at defining truth and must be a critical component of planning. Planning must be an iterative process given the current and even more substantial future system uncertainties.

A wealth of new data on PM_{2.5} constituents will be made available on a routine basis with the implementation of the speciation networks. Previously, detailed aerometric data of this type have only been collected on a national scale in rural environments (i.e., CASTNet and IMPROVE) or as part of special studies of just a few days or months duration. The availability of routinely collected speciation data will enable a range of analyses which have not been possible until now. Results of these analyses are anticipated to provide air quality managers with valuable information on:

- ▶ The important chemical constituents and associated emission sources of fine particulate and their influence on elevated PM_{2.5} mass levels.
- ▶ Trends in mass component concentrations and related emissions, including from specific source categories.
- ▶ Effectiveness of implemented control strategies.
- ▶ Possible errors in emission inventories, emission factors, and speciation profiles .
- ▶ The relative impact of PM components and precursors transported into and out of an air basin from upwind or downwind sources.
- ▶ The effects of atmospheric constituents on visibility impairment and regional haze.
- ▶ Population exposures to certain toxic components of PM_{2.5}.

Insightful analysis of speciated PM data requires a clear understanding of the goals of the analysis (i.e., a precise statement of the questions to be answered by the investigation), familiarity with the range of possible analysis techniques and their individual advantages and limitations, and

the ability to properly interpret the results. Detailed information of this type is beyond the scope of this Section. Instead this Section seeks to illustrate the intended value of the speciation measurements, to present a framework for data interpretation and use, to contrast the roles of States and EPA in analysis activities, to highlight some of the relevant tools, and to accent the link between data use and network design.

2.1 Data Analysis Guidance and Training

EPA has established a ‘virtual’ work group on the Internet to facilitate the development of practical guidance using real world examples for the overall PM_{2.5} program. State and local environmental agency staff as well as consortiums and other environmental groups (such as NESCAUM, MARAMA, WESTAR, LADCO, A&WMA, and STAPPA/ALAPCO) are encouraged to participate in this web-based group; the Internet URL is

<http://capita.wustl.edu/PMFine/>.

In the virtual work group, analysis topics are broken into the following components: Resources, Status & Trends, Attainment Issues, Source Attribution, and Control Strategies. Subgroups have been (or will soon be) formed for each of these subjects areas. As a product of the ‘virtual’ collaborative effort, EPA intends to issue initial PM_{2.5} data analyses guidance in the form of a workbook in late summer 1999. The work groups or hybrids of them will continue to function, however, and the web site and workbook will continue to evolve over time. A dynamic web-based version of the workbook also will be maintained. An initial workshop addressing the overall PM_{2.5} program objectives and introducing the initial draft guidance is tentatively scheduled for September 1999; feedback and additional input will be solicited on the guidance document at that time. A series of subsequent regional based workshops are envisioned for FY 2000 and 2001. Demonstrations and training for analysis tools will be an integral part of all the workshops; more detailed videotaped broadcasts are being considered. An additional EPA web site has been initiated at

<http://www.epa.gov/oar/oaqps/pm25/>

to help disseminate vital program information (such as guidance and on training opportunities). This site consists of topics such as General Information; Publications, Papers and Reports; and Data Analysis Support. The site will provide direct links to PAMS data analysis, Toxics data analysis, and the Virtual Work Group web site described above.

The purpose of this “Data Analysis” section is to present a framework for data interpretation and use. Accordingly, portions of it draw strongly from the current working outline of the virtual work group workbook. The forthcoming detailed “guidance” is not intended as a prescriptive cookbook which the States are dictated to follow. Rather, EPA seeks to present a variety of ideas of how the PM_{2.5} data can be useful for developing and assessing emissions control strategies. Although many apparently disparate methods address similar objectives, the use of redundant techniques with resulting agreement leads to further confidence in the analytic methods and conclusions.

2.2 General Conceptual Flow of Data Analysis Activities

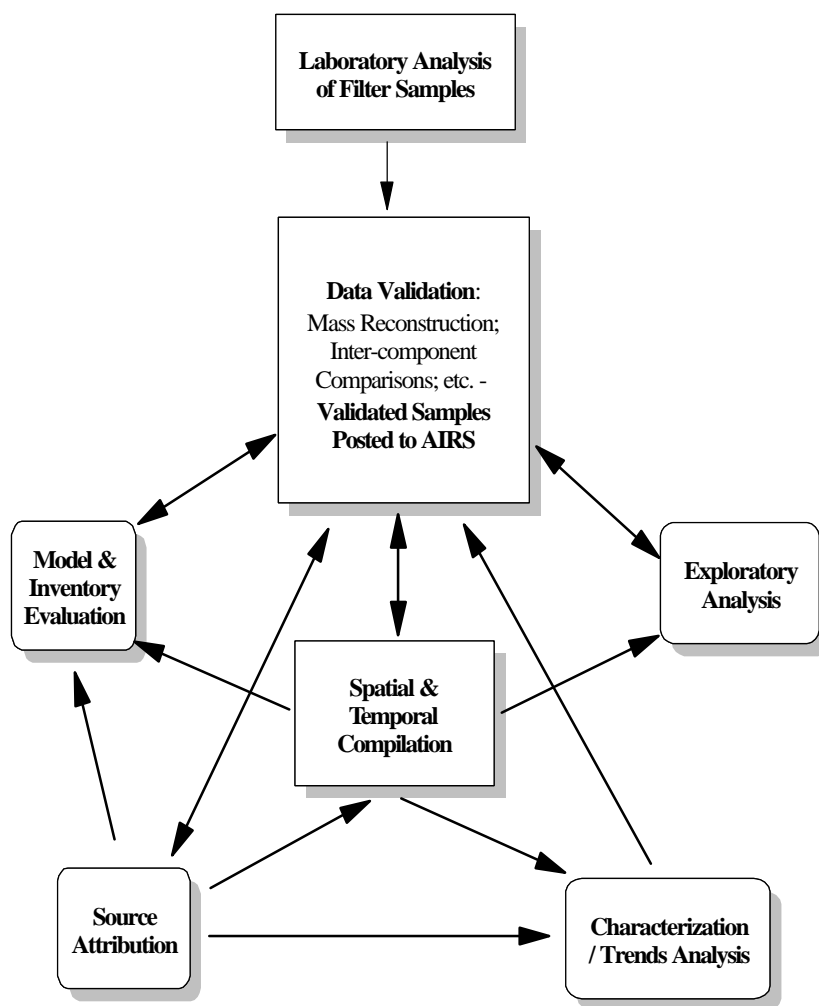


Figure 2-1. Data analysis flow diagram

Common data processing steps for speciated aerosol data are depicted in Figure 2-1. Note that this flow is conceptual and for illustrative purposes only; variations (additional paths, diverse breakouts, etc.) are possible. Following laboratory analyses of filter samples, the speciated data will be validated. A core check of data reasonableness is then developed through mass reconstruction. In this process, the total PM_{2.5} mass is reconstructed by aggregating individually measured components. Typically, this initial reconstruction for a particular sample reflects an atmospheric composition for a single 24-hour period in one location. The result often is simply tabulated or presented graphically to illustrate the

fractional contributions of individual components. This step incorporates some internal quality control. Reasonable comparisons (acknowledging discrepancies due to sampling and filter artifacts) to gravimetric mass should be expected, ideally resulting in greater confidence that the laboratory analyses and associated filter handling have acceptable system accuracy. Inter-component comparisons should also be performed to further affirm data validity. After validation, the data stands as an end product for exploration and policy relevant analyses (e.g. source attribution evaluations or event based emissions inventory comparisons) or can be expanded over greater spatial and temporal frames for further analysis. The time and spatial scales of interest partially dictate the degree of aggregation.

The annual PM_{2.5} standard suggests that yearly aggregation of data might drive many analyses. However, the principal SIP modeling and emission inventory tools operate over highly resolved time periods (e.g., hourly intervals). Accordingly, both time aggregate and time resolved applications should be performed. Relatedly, the expansive regional domains of air quality models, and the recognition of interacting spatial scales, suggests that many analyses should consider multiple monitoring locations. Spatially, temporally, and/or spatially-and-temporally aggregated data are necessary for trends evaluations and are also valuable for inventory and model evaluations. Ambient data apportioned to sources can help quality assure emission inventories and models. Trends in source-apportioned data are beneficial for evaluating control strategy effectiveness. Exploratory analyses are performed on individual samples and aggregated data. Feedback paths to data validation are present from every analysis activity since in-depth evaluations almost always lead to further refinement of the raw data. And, refinements to raw data always should be carried back to AIRS. The specific data analyses activities are described in somewhat more detail in the next section.

2.3 Data Analysis Activities

The data collected by an ambient air network are of little use unless analyzed. Thus, data analysis activities should be an integral part of a State's PM_{2.5} Implementation Plan. Although data collection precedes analysis and interpretation, an understanding of the eventual use of the data must drive the design of the data collection program. This is especially relevant to the non-routine portion of the speciation network which is more flexible. Additionally, analyses will be performed at various levels including State and local agencies, consortiums, Regional Offices, ORD, and OAQPS/EMAD.

All of these need to be coordinated to ensure the most efficient and appropriate use of the data to meet the specified program objectives. A brief description of the currently-envisioned potential uses for speciation data and related activities are discussed below. Note that there exists

a significant amount of overlap among the listed topics and that different breakouts could be equally appropriate. Substantially more detail will be provided in forthcoming guidance.

2.3.1 Data Validation

Although by itself it is not a major policy-relevant data analysis activity, data validation is a requisite building block for all analyses. The quality and applicability of data analysis results are directly dependent on the inherent quality of the raw data itself. Although EPA and reporting organizations will employ rigorous quality assurance and validation measures to insure optimum data quality, errors are still bound to pass through the system. This is especially likely with the new and complex speciation monitoring and sample analysis methods being employed. Quality system requirements for PM_{2.5} speciation sampling and analysis are documented in Section 8 of this document and data validation is addressed in Section 9. In that Section, a four-level data validation system is suggested for the speciated data. The full-service contract laboratories will conduct at least a Level I validation on samples they analyze. To assure national consistency, States will submit (at a minimum) samples from the trend sites to these contract labs. States will be responsible for the additional levels of validation for the samples submitted to the national laboratories. For samples not submitted to the labs, States will be responsible for all levels of validation. EPA is sponsoring development of a software data validation tool, called PMDat, to assist with data validation tasks. This software will be modeled after the VOCDat package which is currently in use by many PAMS reporting organizations to validate their volatile organic carbon (VOC) species data. PMDat will utilize time series, scatter, and 'fingerprint plots' to help identify suspect data points. PMDat will also derive a 'reconstructed' mass total for comparing to various other mass measurements (e.g. gravimetric mass total, collocated FRM, collocated PM₁₀). PMDat is not the only data validation alternative. Commercially off-the-shelf (COTS) statistical software packages (e.g. SAS, S-PLUS, Statistica, etc.) and custom-coded applications can also be used to perform similar validation tasks, as well as additional types of QA checks such as spatial mapping and pure statistical 'outlier' tests (e.g. standard deviations or confidence intervals). Data validation methods documented in the PAMS 1996 Data Analysis Results Report (EPA, 1996c) for PAMS data are equally relevant for the data that will be generated at the PM_{2.5} speciation sites. EPA will issue periodic reports describing the quality of the data collected by the PM_{2.5} network.

2.3.2 Exploratory Data Analysis

There is a fine line separating data validation and data exploration. Although there are differing goals for the two tasks (i.e., the goal of validation is to remove invalid data or qualify suspicious data; the goal of exploratory analyses is to understand the data set and problem better),

the methods incorporate similar attributes. One way to explore a particular data set, is simply to plot the raw data in a variety of standard formats (temporally/seasonally, species-to-species, species-to-total, etc.) such as mentioned in 2.3.1 above. Thus, the PMDat package will be a viable tool for some types of exploration. In addition to PMDat, EPA also has developed AMDAS to facilitate exploratory analysis. AMDAS (Ambient Monitoring Data Analysis System), is an enhanced and renamed version of the existing PAMSDAS (PAMS Data Analysis System) package. Release of the AMDAS tool is anticipated in January, 1999. The AMDAS / PAMSDAS tools are add-on modules for the COTS statistical package S-Plus.

Exploratory analysis can include initial probes or tests of more refined objectives-based hypotheses. Exploratory analyses can be viewed as an activity area wherein ideas develop and evolve to inform other analysis areas such as validation or compliance-type issues. One example of a question that needs to be explored early in (if not prior to) the speciation program is, can we reconstruct PM_{2.5} mass concentrations from speciated concentration data?" Once we know the 'answer' to this exploratory question, we may be able to construct a validation test to identify questionable or invalid data points. Additional analysis of cases where reconstructed mass does not compare well with FRM or other mass measurements (using previously determined formulae) can perhaps point to unusual compliance-related conditions that exacerbate PM_{2.5} loading. Other examples of exploratory questions that will need addressed through speciated data include:

- ▶ PM_{2.5} chemical characterization: What are the chemical components of the fine particulate matter?
- ▶ PM_{2.5} physical characterization: What is the particle size and morphology comprising the fine particulate matter?
- ▶ Pollutant interactions: What are the interactions between PM_{2.5} versus ozone, wet deposition, toxics, greenhouse gases. What are the interactions between VOCs and organic aerosols?
- ▶ What are the meteorological conditions that are conducive to PM_{2.5} formation, accumulation, and removal.
- ▶ What are the impacts of natural sources of PM_{2.5}, such as, biogenics, wildfires, dust on measured levels of PM_{2.5} constituents?
- ▶ What are the origins and potential controls of organic aerosols?

- What are the fundamental differences in formation, accumulation, and removal of PM_{2.5} in the Eastern U.S. versus the Western U.S?

There are several important points that should be made about the above “idea” list:

- 1) Exploratory analyses spans all facets of data analyses and data utilization.
- 2) A logical extension of exploratory analyses is data characterization. Characterization generally entails spatial and/or temporal aggregation, or even further types of binning such as by meteorological conditions. Characterization establishes data expectations. It is a fundamental and requisite first step to accomplishing subsequent data objectives such as trends evaluations and checks of control strategy effectiveness. A baseline must be establish before comparisons can be made against it. PM_{2.5} data characterization is discussed further in Section 2.3.3
- 3) The EPA prescribed speciation trend network will not provide all the information necessary to adequately evaluate even the short (albeit ambitious) list above. Particle size distribution data, for example, will not be determined routinely. However, this information will enhance our understanding of the particle size and morphology comprising the fine particulate matter and such understanding might lead to improved source apportionment techniques which might aid in the development of attainment strategies. States will need to design complementary non-Trend networks that have an objective-based design. The EPA-stipulated number (of 250 non-trend sites) is not ‘etched in stone’. EPA will consider State plans that have augmented sampling at Trends sites in leu of a separate ‘non-Trends’ site. Special studies, especially in the early implementation period may also be favorably viewed. Supersites can also play a role with specialized, higher resolution, and/or more intensive monitoring, however, that program will only encompass a handful of sites and only operate for a limited time frame.

2.3.3 Data Characterization and Trends

The range of this analysis activity includes the spatial, temporal, and compositional patterns of PM_{2.5} concentrations and the influences that changes in meteorology or emissions may have on these patterns. As mentioned in Section 1, one of the primary objectives of the PM_{2.5} chemical speciation program is to provide “Annual and Seasonal Spatial Characterizations of U.S. Aerosols”. Although little is known about the chemical characterization of the PM_{2.5} mass data in urban areas, there are an increasing number of literary references. The guidance will document some of these historic, recent, and ongoing studies, but unless the information presented (or other current analyses produced by or for a reporting organization) is particularly relevant to a given area, States should ‘start from scratch’ with the new speciation program data. The Trends sites should be given the highest priority for initial characterizations since 1) they will be on-line first,

and 2) the monitoring devices will all be comparable (hence facilitating site-to-site and area-to-area comparisons). Characterizations for the speciation data will frequently concentrate on the relative contribution of species details to total mass. ‘Seasonal’ characterizations can be generated for calendar quarters, traditional season definitions (fall, winter, summer, spring), or other time periods found to exhibit similar characteristics. The calendar quarters (Jan-Mar; Apr-Jun; Jul-Sep; Oct-Dec) are important since the annual PM_{2.5} mass NAAQS is based on a weighted quarter average. Special, approved monitoring exceptions should be reflected in the levels of aggregation.

The second ranked speciation program objective (as designated in Section 1) is “Air Quality Trends Analysis and Tracking of Control Programs”. The annual trends in PM_{2.5} constituents will be analyzed to track progress in solving PM_{2.5} air quality problems. Various statistics and indicators (such as component to mass ratios) may be appropriate and will be described in initial guidance. To ascertain true PM_{2.5} and component trends, it may be necessary to adjust the data for meteorological conditions as is often done for ozone. EPA is currently exploring this issue.

It will be several years before there is a sufficient amount of data to construct trends from the speciation data; since a minimum of 3 years is needed to establish a 'trend', these type of evaluations will probably not be possible until 2002 or later. The first few years of data, however, can be used for comparative purposes such as inter-season, episode versus non-episode (high mass percentile vs low mass percentile), divergent meteorological condition, and geographic area comparisons. National scope analyses such as more robust East versus West comparisons (and the culling of associated policy ramifications) will be performed by EPA. Also, since most speciated particulate data available now is from rural environments, comparing the urban-based trends network data to this existing rural centered information will be another early EPA endeavor. The EPA will describe these characterizations, as well as national scope trends (once a sufficient bank exists in various reports such as the annual *National Ambient Air Quality and Emissions Trends Report* (U.S. EPA, 1998e).

As mentioned, the first set of sites put in operation will be the National Trends network of approximately 54 sites. Because of

Table 2-1. Status and Trends Working Outline from the Virtual PM_{2.5} Workbook

(<http://capita.wustl.edu/PMFine/>)

Workgroup/Status&Trends/Outline/S&TOutline.html)

I. Resources

- A. Data
- B. Tools
- C. Historical Literature
- D. Web Links

II. Data Processing

- A. QA Review
- B. Data Screening & Aggregation
- C. Data Updates

III. Temporal Patterns

- A. Diurnal
- B. Day-of-Week
- C. Episodic
- D. Seasonal
- E. Long-Term

IV. Spatial Patterns

- A. Urban
- B. Urban/Rural
- C. Elevational
- D. Regional
- E. National/International

V. Compositional Patterns

- A. Fine Mass
- B. General Species
- C. Detailed Species

VI. Discerning Influences

- A. Meteorology
- B. Emissions
- C. InterPollutant Relationships
- D. Natural Events

VII. Feedback Loops

- A. Data Processing
- B. Network Design
- C. Attainment Issues
- D. Source Attribution
- E. Control Strategies

their placement (in high emissions areas), their similar instrumentation, and their timing (first implemented, thus they will always have the longest data record), these sites will be the best suited for trends and comparison purposes. Data from these sites can eventually be complemented by data from the non-Trends sites; however, the effect of differences in sampling and analysis equipment and techniques on the data must be considered. A variety of statistical techniques are available for comparative and/or trend detection purposes. Examples include t-tests, F-tests, linear regression, analysis of variance, Spearman's rho, Kendall's tau, Theil/Sen slope estimator, etc. Many of these techniques were discussed in a PAMS related document, ***Recommendations for Analysis of PAMS***, (U.S. EPA 1994) and are equally appropriate for the PM_{2.5} speciated data. These techniques will be addressed in future EPA guidance but are well beyond the scope of this Section. The AMDAS module mentioned earlier will include several valuable options for characterizing and summarizing speciated data. A trend detection and display facility will also be available.

Table 2-1 shows the current Status and Trends working outline from the virtual PM_{2.5} workbook work group. The outline and corresponding sub-work group are concerned with all PM_{2.5} program data, not just the speciation data. Accordingly, some aspects of the outline may pertain exclusively or chiefly to mass data. Also, the outline structure is admittedly not extremely detailed nor intuitive; the work group is itself trying to define each of outline items.

2.3.4 Tracking Progress of Control Programs

Once control measures are implemented, either nationwide or in certain nonattainment areas, the speciation network will provide the information necessary for verifying the efficacy of those strategies. This analysis activity has Status & Trends, Source Attribution, and Emission Inventory Evaluation facets to it. Individual specific strategies or an entire suite of activities (such as stipulated in a SIP) can be evaluated to ascertain progress. Control strategy effectiveness checks can encompass simple before-after comparisons (i.e. significance tests of difference) of a parameter's annual mean (or a species to mass ratio); similar comparisons of annual relative contributions of a particular species from a particular source category; or in-depth trends analyses for a particular indicator. PM_{2.5} SIPS may eventually contain emission reduction targets for key PM_{2.5} components and precursors similar to the previous VOC 15% (RFP) plans. The speciated PM_{2.5} ambient data are needed to corroborate the realized emissions reductions. Although "Tracking Progress of Control Programs" sounds like a far-off distant activity which might not start until 2003 or so, such opportunities might be available much sooner. Because many environmental programs and control strategies have multiple goals, serendipitous side effects, and sometimes unforeseen negative consequences, the effect of such programs may be evaluated far

before any specific PM_{2.5} controls are even enacted. States need to be cognizant of all implemented ambient controls and their possible outcomes.

2.3.5 Source Attribution

The PM_{2.5} mass monitors will identify the regions of the country with high PM_{2.5} concentrations. The speciation network will be used to determine which constituents contribute to the high mass concentrations. Source attribution not only helps identify 'what' is causing the (PM_{2.5}) problem, but also addresses the question: 'Who' or 'what' is causing my problem? The scope of this question ranges from general identification of PM-Fine mass fractions which result from local and regional source influence, to the quantitative identification of PM-Fine concentration and composition resulting from specific local and regional sources. As seen in the latter task (quantitative identification), speciation data can also provide information on 'how much' a particular source or source area is responsible for a specific PM_{2.5} episode, its components, or its precursors. Source apportionment information will critically aid the development of strategies for controlling PM_{2.5}. Although the PM fine components collected at the Trends sites are useful for source attribution, finer time resolution measurements are preferred. States will need to address the time interval limitation and opportunity with their non-Trend network designs. Speciation monitoring equipment are perfectly capable of collecting samples of less than 24 hours (e.g. 3-, 4-, or 12-hour). However, if too short of interval is monitored, the concentration of components may be too small (i.e. less than the detection limit) to be of value. With shorter intervals some tradeoffs can be made by increasing the flow rate or using smaller filters. Without these adjustments, a good compromise (for the non-Trend sampling, of course) may be to collect two 12-hour samples, one during the daylight hours (e.g. 6am-6pm) and one at night (e.g. 6pm-6am). Real-time speciation monitoring is also possible and should be considered for non-routine NAMS.

A variety of tools and techniques are available for source attribution / source apportionment. These methods range from simple pollution-rose plots to complex meteorological trajectory models; multivariate and mass balance receptor models; optical microscopy; and combinations thereof. Pollution roses use concentration data (e.g. a PM_{2.5} speciated component) with co-located or nearby-monitored wind direction data, to produce a graphical plot that shows (theoretically) the source direction and associated relative strength for that parameter. There are at least two versions of EPA-supported pollution rose plots that will be available to PM_{2.5} State analysts. An AIRS-Graphics version has been in production for several years on the IBM mainframe but has inflexible input limitations. This plot (and so the entire system) will soon be ported to a UNIX / Internet platform and some enhancements (such as input flexibility) are being requested. The new AIRS-Graphics pollution rose is expected to be in production around July

1999. The S-Plus based tool AMDAS will also contain a pollution rose plot. Because a 10 meter meteorological tower is required at each of the Trends sites, these sites will provide the necessary wind data for these inputs. Meteorological trajectory models are also useful aids in determining an air parcel's source region. These tools, however, require extensively more meteorological data than will be monitored at the speciation sites. External data can be utilized with these analysis tools, and thus their application is recommended for corroborating other aerosol-based methods. An example of a publically available trajectory model is NOAA's HYSPLYT, which is available from NOAA's Real-time Environmental Applications and Display sYstem (READY); a link to this tool is provided on the virtual workgroup web site.

Receptor models are perhaps the most valuable of all source attribution tools. Receptor models use the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations. Receptor models are generally contrasted with dispersion models that use pollutant emissions rate estimates, meteorological transport, and chemical transformation mechanisms to estimate the contribution of each source to receptor concentrations. The two types of models are complementary, with each type having strengths that compensate for the weakness of the others; see next section on Air Quality Model Evaluation. One class of receptor models include principal components and factor analysis, cluster analysis or other multivariate statistical techniques. Factor analysis is a method of decomposing a correlation or covariance matrix. Cluster analysis procedures are also used to detect natural groupings in data. In general, a grouping can be either exclusive (i.e., does not allow the same object to appear in more than one cluster) or hierarchical (consists of clusters that completely contain other clusters). Although numerous air pollution analysis experts have devised useful custom-coded receptor models (using SAS, S-Plus, MATLAB, Fortran, etc.), only a limited number of these are ever 'packaged' for public use. An upcoming multivariate receptor modeling tool that shows significant potential and may soon be available for public use, is the UNMIX package created by Dr. Ron Henry of the University of Southern California. UNMIX interprets a time series of ambient data (PM components, VOC species, etc.) to estimate the number of emission source types impacting a site, the source compositions, and the source contributions to each sample. UNMIX is a new rendition of SAFER (Source Apportionment by Factors with Explicit Restrictions). Unlike the Chemical Mass Balance package (CMB8, discussed below), UNMIX does not require prior knowledge (and profiles) of the sources that impact the receptor; it can, therefore, be used to identify sources missing from the inventory. The EPA Office of Research and Development (ORD) is presently evaluating UNMIX with PM-fine data sets from Phoenix, Baltimore, Fresno, and Seattle; initial feedback is positive. Dr. Phil Hopke of Clarkson University is also developing several promising source attribution applications, and one in particular, Positive Matrix Factorization (PMF) - an allegedly better factor analysis method, has kindled some EPA interest (Hopke, 1998).

OAQPS/EMAD intends to intercompare various source apportionment techniques (UNMIX, Hopke methodology, CMB8 mentioned below, and whatever else looks promising) over the next year. Conclusions and recommendations will be reflected in future PM_{2.5} data analysis guidance and EPA support.

CMB is another type of receptor model and is perhaps the most widely used receptor modeling applications due to its proven history and user-friendly ‘packaging’. The CMB utilizes a sophisticated least squares statistical method for identifying the most likely source categories to a given ambient sample, based on the relative amounts of each species present in the sample, and the relative amounts of those same species present in the emissions of source categories. The newest version of CMB (CMB8, a Windows application) and User’s Manual will soon be posted on EPA’s Support Center for Regulatory Air Models (SCRAM) web site; once there, a link will be set on the Fine Particulate Analysis Workbook site. A draft of a key CMB8 guidance document, ***CMB8 Application and Validation Protocol for PM_{2.5} and VOC*** (U.S. EPA, 1998f), is already posted on the virtual workbook web site; PM_{2.5} application examples contained in that document (or along those lines) will be highlighted in the August guidance.

Optical microscopy, or polarized light microscopy (PLM), is another method for distinguishing atmospheric aerosols and their source. The source of individual particles is determined by characterization of the following properties: morphological, optical, physical, and crystallographic. PLM does not require particle removal for analyses and source sampling is not a prerequisite. PLM can distinguish flyash from soils/pavement; biologicals; and raw coal, coke, and partially pyrolyzed coal. PLM will be addressed in more detail in future guidance.

Scanning Electron Microscopy (SEM) is a related method, whose superior size resolution allows examination of submicron particles. When combined with energy dispersive x-ray fluorescence (SEM/EDX) the method can determine the elemental composition of individual particles, as well as their size and shape. PLM and SEM will be addressed in more detail in future guidance.

Table 2-2. Source Attribution Working Outline from the Virtual PM_{2.5} Workbook (<http://capita.wustl.edu/PMFine/Workgroup/SourceAttribution/Outline/SAOutline.html>)

Outline/SAOutline.html)

I. Resources

- A. Data (PM_{2.5}, emissions inventories & profiles, meteorology, other pollutants)
- B. Source Attribution Tools and Techniques
- C. Training and User Groups
- D. Literature References

II. Data Processing

- A. Q/A Review
- B. Data Screening, Aggregation and Fusion
- C. Treatments for MDL and Measurement Error
- D. Data Formats for Source Attribution Tools

III. Discerning Local vs. Non-local Source influence

- A. By Species (mass, sulfates, organics, nitrates, soil, etc.)
- B. Over Time (annual, seasonal, weekday, episode, diurnal, long term trend)
- C. Over Space (define "local" as function of monitoring network)

IV. Discerning among Source Categories

- A. Natural vs. Anthropogenic (by species, time and space)
- B. Anthropogenic Source Categories (wood smoke, utilities, automotive, etc. - by species, time and space)
- C. Refinement of B (proscribed burning vs woodstoves, oil vs coal utilities, Motor vehicle exhaust vs evaporative vs diesel, fugitive dust, etc.)

V. Discerning among Source Regions

- A. By Direction from receptor(s)
- B. By distance from receptor(s)
- C. By location (distance and direction)
- D. By regional "fingerprint"

VI. Discerning Specific Source Influences

- A. Within local jurisdiction(s)
- B. Beyond local jurisdiction(s)
- C. Changes over time, space or species

VII. Assessing and Reducing Uncertainties

- A. Influences of Emissions vs. Meteorology
- B. Receptor Model Performance Evaluation
- C. "Representativeness" of Short-term Results
- D. Tracers of Opportunity (in space, time, species)

VIII. Emission Profiles and Inventories

- A. Validating Emission Profiles and Inventories
- B. Improving Emission Profiles and Inventories
- C. Estimating Emission Profiles and Inventories
- D. Identification of Unusual Events

IX. Feedback to Network Design (Current and Future)

- A. Identifying and Reducing Uncertainties in Source Attribution
- B. Routine & Enhanced Measurements for Source Attribution
- C. Improving Emissions Profiles and Inventories
- D. Identifying Inefficient/Redundant Measurements

Table 2-2 shows the current Source Attribution working outline from the virtual PM_{2.5} workbook work group. As noted for Status and Trends, the outline and corresponding sub-work group are concerned with all PM_{2.5} program data, not just the speciation data, and thus some aspects of the outline may pertain exclusively or chiefly to mass data. Parties interested in participating in the source attribution (or any of the workbook) work group are encouraged to visit "<http://capita.wustl.edu/PMFine/>".

2.3.6 Air Quality Model Evaluation

The speciation network will provide the data necessary to compare the concentrations predicted by the air quality models to the ambient concentrations at various levels. Such comparisons will be useful for identifying ways to improve the air quality models and will also aid in evaluating the emissions inventories that are integral to the modeling process. Speciated data play an especially important role as the deterministic models predict exact chemical components which can be compared to some of the specific measured analytes. However, the analysis must be tempered with the knowledge that surface point sampling systems, whether measuring exact "gases" or complex aerosols, reflect space and time frames that may not be compatible with averaging schemes used in models. The sampling complexity of aerosols adds greater complexity to model-observation comparisons.

There are at least two EPA modeling systems that will play a near term significant role with fine particulate, the Regulatory Modeling System for Aerosols and Deposition (REMSAD), and the Community Multi-scale Air Quality (CMAQ) model. The REMSAD system is built on the foundation of the UAM-V regional air quality model. An integrated photochemical module provides an active link between oxidant levels and secondary particulate formation. The REMSAD system can be applied at scales ranging from a single metropolitan area to a continent containing multiple urban areas. The model is usually run for multiday period, typically a full year. As such, model comparisons will generally be made to aggregated ambient data. In addition to comparing mass levels, comparisons can also be made for elemental and organic carbon, and a fine particulate remainder; a recent such comparison relied on data from the CASTNet and IMPROVE programs. The Trends site data may be acceptable for future comparisons. Comparisons of modeled versus ambient levels of cadmium, total sulfate, particulate nitrate, ammonium nitrate, and mercury are also plausible. Additional species concentrations from the chemistry module could be extracted from REMSAD if they proved to be important for interpretation of the model results. CMAQ is part of the Models-3 open system framework, and has integrated meteorology, emissions, and transport processors. Like REMSAD, CMAQ is a multi-pollutant model (PM_{2.5}, ozone, visibility, and acid deposition); CMAQ, however, utilizes a full-blown ozone photochemistry module, not a reduced-form one as

incorporated in REMSAD. ORD will perform a diagnostic evaluation of the CMAQ:Models-3 PM_{2.5} capabilities beginning in summer 1999. Model evaluation is inherently an EPA function, especially in the early implementation (models and monitoring) period. States, however, need to produce and appropriately caveat, the necessary (quality assured) ambient data. Once PM_{2.5} models are dictated for regulatory purposes and 'modeled attainment demonstrations' are required, States may take a more proactive interest in model performance.

2.3.7 Evaluation of Emission Inventories, Factors, and Speciation Profiles

One of the key inputs to the aforementioned models are emission inventories. PM_{2.5} speciated data will prove an invaluable aid in evaluating emission inventories and related emission factors and speciation profiles. Both mass data and its components will play an important role in the evaluation of inventories. Because mass can be 'reconstructed' from the speciated data, and because other mass totals will also be generated at the speciation sites (even collocated FRM), mass utilization is discussed here. Ambient-derived ratios of PM_{2.5} mass to other pollutants such as VOC, NO_x, SO_x, and NH₃ (e.g. PM/NO_x) can be compared to similar emissions-derived ratios (for a specific area) to highlight possible discrepancies. Year-to-year and multi-year shifts in ambient mass levels or in ambient pollutant ratios can also be contrasted with the same from the emission inventory. For example: If the emission inventory shows a 10% decline in PM_{2.5} levels over a certain time period, one could check to see if the ambient data also had a similar reduction. Because ambient concentrations are significantly influenced by chemical reactions, as well as mixing height, transport, and carryover effects, it is preferable to make these comparisons using data for morning time periods. This is just another reason that States should consider time resolved measurements in their non-Trend network designs. Also, States need to consider the availability of other pollutant measurements (such as SO_x or NH₃); siting at an existing platform may alleviate this concern.

Speciated data are critical for performing a comprehensive inventory evaluation; emission factors and speciation profiles can not be evaluated without it. Currently, inventories are not routinely maintained (at least not at EPA) for the individual mass components. Thus, to compare ambient speciated data to the inventories, the inventory must be speciated. This should be done with the same system and profiles that are used for model preparation. REMSAD uses the EMS_{2.5} system; CMAQ currently uses MEPPS but will migrate to SMOKE in mid-1999. Emission-derived component and component to mass ratios can then be compared to the ambient data in manners similar to described above for mass. Component grouping (e.g. elements) comparisons may also be appropriate. Significant differences between the ambient and E.I. data can point to problems with emission factors, speciation profiles, temporal allocation factors, or even the spatial allocation method (or related surrogate data). Source attributed data can isolate

the source type (point, area, mobile) or specific categories most out of line. An emission inventory evaluation can and should be complemented with a bottom-up look at those categories that don't match up well. Diurnal ambient data can help validate and improve temporal allocation factors. Enhanced spatial coverage can aid the validation and improvement of the spatial allocation method (and surrogate data). Ambient : E.I. comparisons can encompass large areas but are typically confined to a small number of emissions dominated grid cells. Upwind grid cells can be included in the comparison but are sometimes not given equal weight. Recommendations relating to these issues will be included in the August guidance. States should design their network their speciation networks with emission inventory validation in mind.

2.3.8 Development of Control Strategies

Speciated day will play a vital role in the development of control strategies. In addition to helping 'prove in' the models (F) and validate the model input inventories (G), ambient data also help in other modeling support activities. Ambient data can be used to help define or affirm the modeling domain (area); the boundary ('initial') conditions; and the selection of the modeled episode, season, or year. Analysis of observational (including speciated) data can be used in its own right to suggest strategies, or to corroborate or fine-tune modeled ones. The latest ozone attainment demonstration guidance dictates the following policy, "Provided the modeled attainment test and a supplementary screening test are passed or close to being passed, States may use a broader set of analyses to estimate if attainment is likely. This is called a 'weight of evidence' determination. A 'weight of evidence' determination includes results obtained with air quality simulation models plus conclusions drawn from analyzing monitored air quality data, emissions estimates and meteorological data. Results of each analysis are considered in concert to determine whether or not attainment is likely. At a minimum, a weight of evidence determination should consider the following 3 types of corroborative analyses: application of air quality simulation models, observed air quality trends and estimated emissions trends, and outcome of observational models. Although these statements are drawn from the 8-hour ozone attainment guidance, a similar policy is expected for the new fine particular standard.

2.3.9 Other Analysis Activities

Listed below are several additional analysis activities that should be explicitly mentioned. There is some coverage of a few of these items in the categories above, but they are highlighted again to stress their importance.

- ▶ **Correlation with FRM Mass Concentrations:** Where PM_{2.5} mass and speciation monitors are collocated, it will be useful to develop an empirical relationship between the

PM_{2.5} mass observations and the mass concentration obtained from the speciation monitors. Such an analysis will provide information about the comparability of the measurements from the FRM's and from the speciation monitors.

- ▶ **Health Studies:** Speciated PM_{2.5} data will be important to continued epidemiological studies into the health effects of PM_{2.5} and its constituents. The 'every 3rd day' sampling regime of the Trends Sites may not be sufficient for most of these studies, and neither may the non-Trends component; the supersites' design, however, should reflect the health effects community's needs. Some of the monitored target speciation parameters are HAPs or HAPs constituents (selected elements and ultimately some semi-volatile organic compounds). Speciation data can thus be used for toxics exposure assessments, including estimation of risk levels and the size of effected populations.
- ▶ **Transport Analysis:** Speciated data can be used in conjunction with collocated or other available meteorological data to characterize and quantify the flow of pollutants / PM_{2.5} components into or out of a particular region.
- ▶ **Synthesis with Oxidant Data:** At the sites with both PM_{2.5} speciation monitoring and monitoring for oxidant precursors and sinks, it will be possible to perform analyses to investigate the relationships between PM_{2.5} constituents and other important atmospheric constituents to gain better process understanding of both PM_{2.5} and ozone formation, maintenance, and removal. Ozone formation and formation of secondary particulates result from several common reactions and reactants. Often similar sources contribute precursors to both ozone and fine particulate problems. In some regions of the U.S., high regional ozone and secondary particulates have been observed under common sets of meteorological conditions. Reducing fine particulate matter is the principal controllable means for improving regional visibility. U.S. EPA policy is to encourage integration of programs to reduce ozone, fine particulates and regional haze to ensure they do not work at cross purposes and to foster maximum total benefit for lower costs.
- ▶ **Integration with Other Databases:** There are several other databases containing speciated PM_{2.5} data, for example, the data collected through the IMPROVE network, Clean Air Status and Trends Network (CASTNET), and the data used in the numerous health effects studies. It will be important to integrate the data from these various databases to increase the amount of information in one of the networks using the information in these other networks. EPA will support the creation and public posting of integrated data sets.

2.3.10 Section Summary

The key points of this Section are reiterated below:

- ▶ The PM_{2.5} speciation networks will generate data useful for expanded understanding of fine particulate formation and removal processes, general characterization and comparison purposes, trends analysis, source attribution, control strategy development, checks of control strategy effectiveness, emission inventory and model evaluation, and other related uses. All these intended uses are interrelated.
- ▶ The EPA will issue guidance documents detailing potential uses for the PM_{2.5} mass and speciation data. The first iteration of guidance will be issued around August, 1999. These guidance documents will be based on (1) techniques described in the published literature and (2) concepts offered by the State and local agencies, the Regional Offices, and EMAD. After a panel of experts peer reviews each document, the documents will be made publicly available through the Internet.
- ▶ The EPA will sponsor development of tools to assist with some of the analyses described in the guidance documents. Many software packages have already been developed for other criteria pollutants and some may be modified to accommodate PM_{2.5} mass and speciation data. Examples include VOCDat and PAMSDAS. Also, an U.S. EPA web site called PM Fine Data Analysis will be available, consisting of topics such as General Information; Publications, Papers and Reports; and Data Analysis Support. The site will provide direct links to PAMS data analysis, Toxics data analysis, and the Virtual Work Group web site.
- ▶ Training and workshops will be conducted to demonstrate proven data analyses, to present potential limitations of the conclusions from the data analyses, and to demonstrate the software tools that have been developed/modified specifically for PM_{2.5} data analysis. The first national data analysis workshop is tentatively scheduled for September, 1999. Subsequent workshops (planned for FY '00) will be conducted in accordance with the Regional and State and local needs.
- ▶ The EPA will issue periodic reports describing the national trends and the quality of the data collected by the PM_{2.5} network. Trends for mass and key constituents, for example, will be highlighted in the annual National Ambient Air Quality and Emissions Trends Reports.

- ▶ The creation and evolution of the guidance documents, tools, workshops, and reports will be aided by the virtual PM Fine Data Analysis Work Group, an interactive web site that will solicit ideas and comments from the ambient air monitoring and analysis community at large, particularly from groups such as NESCAUM, MARAMA, WESTAR, LADCO, TNRCC, CARB, A&WMA, and STAPPA/ALAPCO. In addition, more focused groups and subgroups comprised of individuals from EMAD, AQSSD, Regions, and States who have expertise in areas such as ambient air data analysis, chemistry, and meteorology will help address specific and pressing issues.
- ▶ States need to consider the goals of the data collection in their network design, especially in the non-Trends portion. These considerations include siting, monitoring schedule (more frequent than every 3rd day and/or intervals less than 24-hours), and availability (collocated or nearby monitoring) of other related pollutant and meteorological parameter data.

2.3.11 Additional References

Additional references to related readings on exploratory and interpretive data analyses are listed below.

Guthrie, Paul; Gao, Dongfen; Mansell, Gerard (1998). Evaluation of the Performance of the REMSAD Modeling System for Fine Particles and Deposition - Final Report, produced for EPA-OAQPS. Systems Applications International; SYSAPP-98/24; June, 1998.

Introduction to Receptor Modeling, APTI Course 424; U.S. Environmental Protection Agency, Air Pollution Training Institute; January, 1998.

Use of Models and Other Analyses in Attainment Demonstrations for the 8-Hour Ozone NAAQS - Draft; U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards; October 1986.

3.0 PARTICLE CHARACTERISTICS AND TARGET SPECIES

The following section discusses particle size distribution, the major constituents of PM_{2.5}, potential source contributions relative to the chemical speciation program, and the target species and their characteristics. For clarification, a table is included in Section 3.3 that provides a matrix of filter type, the target chemical species measured on that filter type, and the analytical technique used to determine the species concentration for samples collected within the routine speciation monitoring network.

3.1 Particle Size Distributions

Atmospheric particles originate from a variety of sources and possess a range of properties. Atmospheric particles contain inorganic ions and elements, elemental carbon, organic and crustal compounds. Some particles are hygroscopic and contain particle-bound water. Particulate matter (PM) is a generic term applied to this broad class of chemically and physically diverse substances that exist as discrete particles over a wide range of sizes. Particles are liquid droplets or solids that originate from a variety of natural and anthropogenic stationary and mobile sources. Atmospheric PM occurs as fine-mode and coarse-mode particles that, in addition to falling into different size ranges, differs in formation mechanism, chemical composition, sources, and exposure relationships. Primary particles are composed of material directly emitted into the atmosphere, while secondary particles form as a result of chemical reactions involving gas-phase precursors or other processes involving chemical reactions. Examples of primary particles include wind-blown dust, seas salt, road dust, and mechanically-generated or combustion-generated particles such as fly ash and soot. An example of secondary particles include sulfate formed from the atmospheric oxidation of sulfur dioxide.

Size is one of the most important characteristics in the determination of the properties, effects and fate of atmospheric particles. Three approaches are used to classify particles by size:

- ▶ modes, based on formation mechanisms and modal structure observed in the atmosphere (e.g., nuclei and accumulation modes which comprise the fine and coarse particle mode;
- ▶ cut point, based on the 50% cut point of the specific sampling device (e.g., PM_{2.5} and PM₁₀); and
- ▶ dosimetry, based on the ability of particles to enter certain regions of the respiratory tract.

Fine and coarse particles are often defined in terms of the modal structure of particle size distributions typically found in the atmosphere. An important feature of atmospheric aerosol size distributions is their multimodal nature. The PM_{2.5}, PM₁₀, and total suspended particulate (TSP) size fractions are ideally measured by air quality monitoring devices by range of size distribution.

The mass collected is proportional to the area under the distribution curve within each range. The TSP fraction ranges from 0 to about 40 μm in aerodynamic diameter, the PM₁₀ fraction ranges from 0 to 10 μm , and the PM_{2.5} fraction ranges from 0 to 2.5 μm . No monitoring device passes 100 percent of the particles below a certain size and excludes 100 percent of the particles above that size. When particulate sampling occurs, each of the size ranges contain a certain number of particles above the upper size designation of each range.

Condensable species can either nucleate to form a new particle (nucleation), or condense onto the surface of an existing particle (condensation). Nucleation results in an increase in particle number and particle mass. Condensation leads only to an increase of aerosol mass and surface area, but does not affect the total number of particles. The “nucleation” range consists of particles with diameters less than $\sim 0.1 \mu\text{m}$, also termed “ultra fine particles,” that are emitted directly from combustion sources or that condense from cooled vapors soon after emission. Nucleation particle lifetimes are usually less than one hour because they rapidly coagulate with larger particles or serve as nuclei for cloud or fog droplets. The nucleation range is detected only when fresh emissions are closest to a measurement site or when new particles have been recently formed in the atmosphere (Lundgren and Burton, 1995). However, ultra-fine particles can persist in the atmosphere if removal mechanisms are weak.

The “accumulation” range consists of particles with diameters between ~ 0.1 and $2 \mu\text{m}$. These particles contains fresh accumulation aerosol emitted from combustion sources, and can also result from gas-to-particle conversion, condensation of volatile species, and finely ground dust. Nucleation and accumulation ranges primarily constitute the PM_{2.5} or “fine” particle size fraction, and the majority of sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, and organic and elemental carbon is found in this size range. The PM_{2.5} accumulation range shows two sub-modes, the condensation mode (containing gas phase reaction products), and the droplet mode (resulting from growth by nucleation and reactions that take place in water droplets). When these modes contain water soluble particles, their peak will shift toward larger aerodynamic diameters as the humidity increases.

Particles larger than ~ 2 or $3 \mu\text{m}$ are called “coarse particles” that result from grinding activities and are dominated by material of selective biological, geological, and man-made origins (pollen and spores, ground up trash, leaves, and tire abrasion). There are certain conditions under which coarse particles are created from secondary reactions in the atmosphere. For example, the coarse nitrate particle fraction in Los Angeles, California, is believed to occur from a reaction of NO_x with sea salt.

Figure 3-1 shows the size distribution of suspended particles measured from common emissions sources (Ahuja et al. 1989; Houck et al. 1989). The data present here are meant to illustrate “rough” average concentrations of individual components. Windblown dust from soil, unpaved roads, construction, evaporation of sea spray, pollen, mold spores, and dusts formed from the grinding of larger particles are predominantly in the coarse particle size range, with minor or moderate quantities in the PM_{2.5} fraction. Fine particulate can be secondarily formed from gases or by chemical reaction or vaporization. Sources of fine particulate include the combustion of coal, oil, gasoline, diesel fuel, and wood, and high temperature processes such as

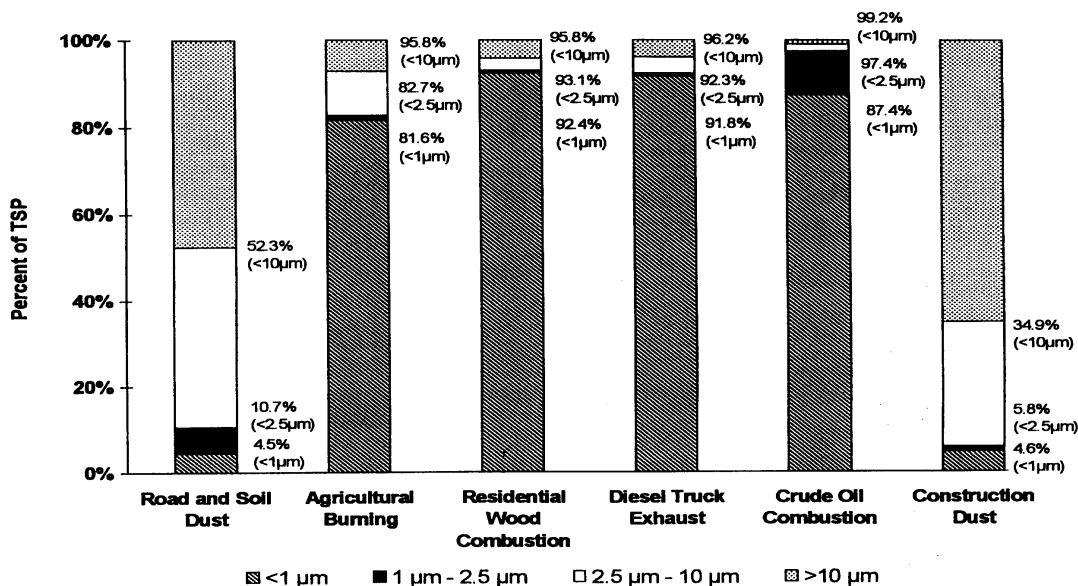


Figure 3-1. Size distributions of several particulate source emissions

steel mills, etc. It is important for network operators and data analysts to understand that at various places and times, any one of the three or four major components can dominate the particulate mass in a 24-hour sample.

3.2 Major Chemical Components and Potential Source Contributions

A variety of suspended particles can be found in the atmosphere; however, there is surprising consistency regarding the major components of suspended particles. As mentioned previously PM_{2.5} is composed of a mixture of primary and secondary particles. Primary and secondary particles have long lifetimes in the atmosphere (days to weeks) and can travel long distances (hundreds to thousands of kilometers). They tend to be uniformly distributed over

urban areas and larger regions, especially in the eastern United States. As a result, they are not easily traced back to their individual sources. The types of particles emitted directly (primary) include soil-related and organic carbon particles from the combustion of fossil fuels and biomass materials. The main sources of soil-related particles are road dusts, construction, and agriculture. The main sources of combustion-related (secondary) particles are diesel and gasoline motor vehicles, managed and open burning, residential wood combustion, and utility and commercial boilers. Combustion processes also emit primary fine particles consisting of mixtures of many trace metal compounds and sulfuric acid mists. The principal types of secondary aerosols are organics and ammonium sulfate and nitrate formed from gaseous emissions of sulfur dioxide (SO₂) and nitrogen oxides (NO_x) which react with ammonia. Gaseous organics from internal combustion engines as well as other combustion sources such as cooking are precursors to secondary organics. Sulfur dioxide, nitrogen oxides, and ammonia (NH₃) are important precursors to secondary aerosols (ammonium sulfate, ammonium bisulfate, ammonium nitrate) and information on their chemical abundance is useful at source and receptor locations to determine causes of high PM_{2.5} levels.

Sulfate, strong acid, nitrate, organic and elemental carbon, trace elements (including metals), ammonium and water are often the major constituents of PM_{2.5}. Major sources of these substances are fossil fuel combustion by electric utilities, industry and motor vehicles; vegetative burning; and smelting or other processing of metals. Sulfur dioxide, NO_x, and certain organic compounds are major precursors of secondary fine particulate matter. The eastern United States has a concentration of coal-burning power plants that emit significant amounts of SO₂, while the western U.S. has relatively low SO₂ emission densities (Malm, 1994). The main source of NO_x emissions are from the combustion of various fuels. Nationwide, about one-half of the NO_x is from stationary sources, while the remainder is from mobile sources such as spark-ignition and compression-ignition engines in automobiles and trucks.

Carbonaceous aerosols are a complex mixture of carbonate, elemental and organic carbon. Ambient studies have shown that carbonate carbon accounts for a negligible fraction of the total carbon in urban aerosol. Due to the great number of compounds with various volatility, the sampling of organic aerosols presents a difficult challenge. Carbonaceous aerosols are usually a major component of fine particulate mass. These particles consist of a multitude of organic and elemental carbon. Thousands of compounds have been identified in the ambient air, but in studies where individual organic compounds have been quantified, the sum of the measured compounds amount for only a few percent of the total organic mass (Bennett and Stockburger, 1994). Organic aerosols in the atmosphere may result from direct source emissions (primary) or condensation of low vapor pressure products of gas phase reactions of hydrocarbons onto existing atmospheric particles (secondary) or the reaction product of primarily emitted organic

compounds with atmospheric oxidants. Elemental carbon is emitted directly from fossil fuel combustion sources.

Most of the PM_{2.5} mass in urban and nonurban areas can be defined by a combination of the following components that are both primary and secondary aerosols:

- ▶ **Sulfate:** Ambient sulfate can be either a primary or secondary constituent. Ammonium sulfate, ammonium bisulfate, and sulfuric acid are the most common forms of sulfate in atmospheric particles. These compounds are water soluble and reside almost exclusively in the PM_{2.5} fraction. Most fine sulfates are produced by oxidation of SO₂ gas to sulfate particles. Sources of SO₂ emissions include coal-burning power plants and copper smelters.
- ▶ **Nitrate:** Ammonium nitrate is the most abundant particulate nitrate compound resulting from a reversible gas-to-particle equilibrium between ammonia gas and nitric acid gas, and particulate ammonium nitrate. Sampling for particulate nitrate is subject to both positive and negative artifacts due to the reversible gas-to-particle phase equilibrium. Because the equilibrium is reversible, ammonium nitrate particles can evaporate into the atmosphere or after collection on a filter, due to changes in temperature and relative humidity. Sodium nitrate is found in the PM_{2.5} and coarse fractions near sea coasts and salt playas where nitric acid vapor irreversibly reacts with sea salt (NaCl).
- ▶ **Ammonium:** Ammonium sulfate, ammonium bisulfate, and ammonium nitrate are the most common compounds containing ammonium. Ammonium sulfate and ammonium bisulfate result from the irreversible reaction between sulfuric acid and ammonia. Ammonium sulfate is present primarily as neutralized ammonium sulfate while ammonium bisulfate and sulfuric acid are not present in great abundance. Atmospheric ammonia (NH₃) is a primary basic gas present in the atmosphere. Significant sources of NH₃ are animal waste, ammonification of humus followed by emission from soils, losses of NH₃-based fertilizers from soils, and industrial emissions. Ammonia can absorb on wet surfaces or react with nitric acid to form ammonium nitrate.
- ▶ **Organic Carbon:** Particulate organic matter is an aggregate of thousands of separate compounds that usually contain more than 20 carbon atoms. Due to the number of organic compounds present, analysis of organic carbon presents a difficult challenge. No single analytical technique can characterize the organic compounds present in the atmosphere. Particulate organic carbon originates from combustion, geological processes, road dusts, and photochemistry. Identification of "organic carbon" is operationally defined by the sampling and analysis methods chosen. Quantification of semi-volatile components of organic carbon depends on the sampling method because the partitioning of semi-volatile compounds can change between the gas and particulate phases during sampling. In

addition, accurate differentiation of high molecular weight organic compounds from the elemental carbon are method dependent as well.

- ▶ **Elemental Carbon:** Particles emitted from combustion sources contain light absorbing elemental carbon, often called “black carbon”. Particulate elemental carbon is a tracer for combustion-derived particles, whereas soil- and marine-derived aerosols contains negligible amounts of elemental carbon. Geological material contains variable abundances. Elemental carbon is present along with organic carbon, and discrimination of particulate elemental from organic carbon depends on the analytical method used. For example, thermal optical analysis methods can incorrectly estimate some of the high molecular weight organic compounds as elemental carbon, because the high molecular weight compounds require a high temperature for volatilization and combustion, and they are sometimes converted to soot before they are quantitated.
- ▶ **Sodium Chloride:** Salt is found in suspended particles near sea coasts, open playas, and after de-icing materials are applied. In its raw form, salt is usually in the coarse particle fraction and is classified as a geological material. When water of fog droplets containing sodium chloride evaporate, many of the “dry” core particles are below 2.5 μm in diameter. Particles that originally contain sodium chloride may be neutralized by nitric or sulfuric acid; the chloride is driven off and replaced by equivalent amounts of nitrate or sulfate. Such particles will be classified as nitrate or sulfate and will be deficient in chloride. Sodium chloride can constitute over 50 percent of the PM₁₀ and 30 percent of the PM_{2.5} at the California coast, which is 5 to 10 times higher than is usually found inland.
- ▶ **Water:** Soluble nitrates, sulfates, ammonium, sodium, other inorganic ions, and some organic material absorb water vapor from the atmosphere, especially when the humidity exceeds 70 percent. Sulfuric acid absorbs some water at all humidity levels. Particles containing these compounds grow into the droplet mode as they take on water. Some of this water is retained as the particles are sampled and weighed. The precise amount of water quantified in the PM_{2.5} mass will depend on the ionic composition and the equilibration relative humidity applied prior to laboratory weighing. Highly acidic aerosols containing sulfuric acid may not give up water, even when the particles are equilibrated at lower relative humidity.
- ▶ **Geological Material:** Suspended dusts consisting mainly of oxides of aluminum, silicon, calcium, titanium, iron, and other metal oxides. The precise combination of these components depends on the geology and industrial processes of the area. Geological material typically consists of 5 to 15 percent PM_{2.5} particles and could be as high as 30 to 40 percent in central California during summer months.

The value of identifying many of the chemical species is, in part, in their use to determine the origins of different air masses. The relative abundance of chemical components in an ambient PM_{2.5} can indicate the chemical composition of the source emissions in the monitored environment. Chemical source profiles are fractional mass abundances of the measured chemical species relative to the primary PM_{2.5} mass from source emissions. Receptor modeling has proven to be a useful method for identifying contributions of different types of sources, especially for the primary components of ambient PM. Apportionment of secondary PM is more difficult because it requires consideration of atmospheric reaction processes and rates. Results from western U.S. sites indicate that fugitive dust, motor vehicles, and wood smoke are the major contributors to ambient PM there, while results from eastern U.S. sites indicate that stationary combustion and fugitive dust are major contributors to ambient PM in the East. Sulfate and organic carbon are the major secondary components in the East, while nitrates and organic carbon are the major secondary components in the West.

Previous chemical profile compilations include chemical abundances of elements, ions, and carbon for geological material (e.g., paved and unpaved road dust, soil dust, storage pile); motor vehicle exhaust (e.g., diesel-, leaded-gasoline-, and unleaded-gasoline-fueled vehicles); vegetative burning (e.g., wood stoves, fireplaces, forest fires, and prescribed burning); industrial boiler emissions; and other aerosol sources. More modern, research-oriented profiles include specific organic compounds or functional groups, elemental isotopes, and microscopic characteristics of single particles.

As fuels, technologies, and use patterns have changed from 1970 to the present, so have the chemical profiles for many emissions sources. Lead has been phased out of U.S. and Canadian fuels, but it is still used in some Mexican gasolines that might affect PM_{2.5} at border areas. Catalytic converters on spark-ignition vehicles, improved compression-ignition engines, and newly-designed wood combustion appliances have substantially reduced carbon abundances in emissions from these small but numerous sources. Similarly, process improvements and new source performance standards have resulted in changes in chemical component emissions from large industrial emitters. Source profiles must be paired in time with ambient PM_{2.5} chemical species measurements to establish a reasonable estimate of what is expected in ambient air.

The spatial and temporal variability of PM_{2.5} profiles are influenced by many factors, including:

- ▶ Source emissions of precursor gaseous and primary particles that are highly variable due to differences in fuel use and process operating conditions.

- ▶ Measurements of the major components discussed above for the PM_{2.5} speciated monitoring network can only provide a first-order source attribution of ambient PM_{2.5} concentrations to major source types. Additional measurements of precursor gases, isotopes, particle morphology, and organics need to be acquired to quantitatively assess the associated source sub-types.
- ▶ Trace metals acquired from elemental analysis of polytetrafluoroethylene (PTFE) membrane filters may be found to be abundant in both anthropogenic and geological source signature profiles. Identifying and quantifying major source contributions are not solely sufficient for source characterization; chemical speciation of ammonium, sulfate, nitrate, organic carbon, and elemental carbon are also essential.

3.3 Targeted Chemical Species

Most of the PM_{2.5} mass in urban and nonurban areas can be attributed to a combination of materials as discussed above. The target species of interest for the PM_{2.5} chemical speciation program are similar to those currently measured within the IMPROVE program. Their selection is based on the chemical speciation program data use objectives, primary constituents of PM_{2.5}, capability of current analytical methods, availability of filter types, and known analytical method performance characteristics.

The target species for this program consist of:

- ▶ anions (particulate sulfate, nitrate) and cations (particulate ammonium, sodium, and potassium);
- ▶ trace elements (about 20 elements from magnesium through lead);
- ▶ total carbon (for the purposes of this document is defined as the sum of organic, elemental, and carbonate carbon) and semi-volatile organic aerosol constituents; and
- ▶ particulate mass.

Although the target list contains chemical species that have been measured in previous studies, particulate organic carbon and semi-volatile organic species are considered to be research-oriented or non-routine in nature. Aerosols include many carbon-containing species with a wide variety of properties; however, most measurement methods identify these as either organic or elemental carbon. The measurement of organic and elemental carbon is operationally-based and dependent on the specific analytical technique used. There are currently no reference standards or standardized method for distinguishing between organic and elemental carbon; therefore, differing results can be obtained for the same sample depending on the analytical method used. Because of this issue, it is extremely important that the same analytical method be

used to determine carbon at the NAMS trends sites for consistency. Although no standards are currently available for the organic and elemental carbon content of particulate carbon from a sample filter, good interlaboratory agreement (Birch, 1998) was obtained between six laboratories using the thermal-optical instrumentation on which the NIOSH method 5040 is based. In previous studies, laboratories using different analytical methodologies obtained variable results, but this can be expected with an operational-based method. The fact that a method is operationally-based does not mean it is not well-characterized or reasonably accurate. When the definition of an analyte is based solely on optical and thermal properties, the analysis is by definition an operational one. In this case, the carbon in widely different types of carbon-containing materials is collectively measured as either “organic” or “elemental” depending on these properties. A single standard is not appropriate when analytes are defined as such. Instead, the relative accuracy of different thermal methods is better addressed by examining the accuracy of total carbon measurements and ensuring that pyrolyzable organic materials used for calibration (e.g., sucrose) have no or little elemental carbon content.

Semi-volatile organic aerosols are included in the target list; however, their determination is outside the current scope of the speciation program and should not be considered on a routine basis due to the research-oriented nature of measuring these species. Promising and novel approaches for reducing artifacts due to sampling are not yet ready for routine deployment; however, research directions suggest that current and future technological developments will permit both extensive quantification of individual compounds and accurate differentiation of semi-volatile gas and particulate phase organic carbon. Therefore, speciation of individual organics and differentiation of the semi-volatile fraction from total carbon is optional. Semi-volatile organic aerosols may be considered for special studies and later added to the routine PM_{2.5} speciation program as the methodology is further developed. Volatilization of semi-volatile compounds is a known source of error for species such as ammonium nitrate and many organics. Evaporative losses of semi-volatile organic compounds can be significant.

Each series of target species requires sample collection on the appropriate filter medium and chemical analysis by methods of adequate selectivity, sensitivity and reliability. The filter substrates used to collect particulate matter are chosen for compatibility with the species collected and the particular chemical analyses. Pretreated quartz fiber filters are used to collect samples destined for determination of atmospheric carbonaceous aerosol concentrations. PTFE filters are employed to obtain atmospheric particulate matter samples for mass concentration determination and for subsequent measurement of a wide variety of major and trace elements and water soluble anions and cations. The nylon filter is used to capture nitrate species. For clarity it is beneficial to think in terms of filter type, the chemical species measured on that filter type, and the analytical

technique used to quantify the species. Table 3-1 provides the filter types, target species, and analytical methods used for the routine NAMS program.

3.3.1 Ions

Ionic species (sulfate, nitrate, ammonium, sodium, and potassium) can represent a large fraction of fine particulate matter, thus their determination is critical in order to meet the data analysis objectives for this program as given in Section 1.2. These ions will be measured at all NAMS speciation sites. The analysis of other important ions such as hydrogen and chloride are optional and may be included at non-routine NAMS depending upon the specific network data use objectives and availability of resources.

Table 3-1
Chemical Speciation Filter Medium, Target Species and Analytical Methods

Filter Medium	Target Species	Analytical Technique
PTFE (Teflon®) filter	Elements and mass	EDXRF (IO-3.3) and Gravimetry
Nylon filter with nitric acid denuder	Nitrate, sulfate, ammonium, sodium, and potassium	IC (National Park Service Method)
Pre-fired quartz fiber filter	Total carbon (including organic, elemental, carbonate carbon)	TOA (NIOSH 5040)
EDXRF - Energy Dispersive X-ray Fluorescence IC - Ion Chromatography TOA - Thermal Optical Analysis		

- **Sulfate:** Sulfate is one of the most robust particulate matter species because it remains stable during and after sampling. Sulfate will be collected on nylon filters and aqueous extracts of these filters analyzed using ion chromatography (IC). It is important to utilize the appropriate denuder for SO₂ gas while making particulate sulfate measurements and to maintain the denuder for optimal efficiency while in use. Particulate sulfur is also routinely analyzed using X-Ray fluorescence (XRF). Measurements of colocated samples by ion chromatography and XRF are usually highly correlated. The typical mass ratio of [(sulfate by IC)/(sulfur by XRF)] is about 3, which indicates that almost all of the fine particle

sulfur is in the form of sulfate. Therefore, for QC purposes routine comparisons may be made between the sulfate concentrations determined using ion chromatography and sulfur concentrations obtained from XRF if available.

- ▶ **Nitrate:** Accurate measurement of particulate nitrate requires the removal of gas phase nitric acid prior to particle collection. It also requires the collection of nitrate on a nylon filter, which binds the nitric acid molecules produced during the volatilization of the collected particulate ammonium nitrate. Nylon filters are slightly alkaline and can collect nitrate quantitatively. Aqueous extracts of the nylon filters will be analyzed using IC to determine the nitrate concentration. Removal of the gaseous nitric acid is achieved by using diffusion denuders coated with alkaline substances (e.g., sodium carbonate) or the use of unanodized aluminum inlets.

Previous methods, which have used PTFE or glass fiber filters, are negatively biased due to ammonium nitrate loss during and after sampling. Loss of ammonium nitrate can be caused by the presence of ammonium bisulfate and similar incompletely neutralized forms of sulfuric acid collected on the filter media (Koutrakis et al., 1992). The equilibrium between particle ammonium nitrate, gaseous ammonia, and nitric acid can also be perturbed by changes in relative humidity and temperature. In addition, nitrate can be lost after sampling during sample transport and storage. To date, there is no agreement among different studies regarding the extent of nitrate loss. This disagreement stems from the fact that these results correspond to a variety of locations, meteorological conditions, and sampling methods. If the speciation sampler relies upon metallic denuders which may be used for long periods of time (e.g., more than a couple of weeks, as with the IMPROVE network), the capacity of these denuders should be determined through laboratory and field studies.

- ▶ **Ammonium:** Aqueous extracts of nylon filters will be analyzed using IC to determine ammonium concentrations. Ammonium sulfate salts are very stable, so ammonium losses during sampling and storage are negligible. However, ammonium nitrate, which is an important constituent of fine particle mass, is unstable and can volatilize during both sample collection and storage as discussed above. The extent of dissociation of ammonium nitrate depends on many parameters, including temperature, relative humidity, and face velocity of the collecting filter. It is anticipated that current sampling techniques underestimate ammonium concentrations due to the volatilization of ammonium nitrate, but fine particle mass contains many acidic compounds and consequently, a fraction of volatilized ammonium (in the form of ammonia) can be retained on a PTFE filter by reaction with the acid compounds. Therefore, it is reasonable to assume that ammonium loss will be less than the nitrate loss.

- **Potassium and Sodium:** These two cations can be used to trace wood burning and ocean sources, respectively. Similarly, as for the rest of the ions, aqueous extracts of nylon filters will be analyzed using IC to determine the concentrations of potassium and sodium. Many precautions must be taken during the filter preparation, sampling, transport, and analysis to minimize sodium contamination of the samples. Otherwise, both laboratory and field blanks will be highly variable, and sampling precision poor.

3.3.2 Elements

Elemental analysis of aerosol samples is important because it can be very helpful in identifying particle sources, and in determining the contribution of the soil and ocean sources to fine particle mass. The contribution of trace metal salts (oxides, nitrates, and sulfates) may also be determined, but typically they are expected to be negligible. To date, several analytical methods have been used to determine the elemental composition of particulate matter. X-Ray Fluorescence (Dzubay and Stevens, 1975; Jaklevic et al., 1977) and Proton Induced X-Ray Emission (Cahill et al., 1990) have been used extensively in the analysis of ambient aerosols because they are non-destructive, have multi-element capabilities, and are relatively low cost. X-Ray Fluorescence (XRF) is the analytical method chosen for the chemical speciation program. This technique is performed on PTFE (Teflon®) filters and determines the concentration of approximately forty elements (from sodium to uranium); however, for typical atmospheres, the analysis is useful only for half of these elements, including aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, arsenic, selenium, bromine, cadmium, and lead.

3.3.3 Carbonaceous Aerosols

Accurate mass balance and quality assurance require determination of particulate (total) carbon (C_t), because of its abundance. Differentiation of organic (C_o), elemental (C_e), and carbonate carbon (C_c), provides more useful characterization for trends analysis and source attribution. For the purposes of this guidance document, we define total carbon as $C_t = C_o + C_e + C_c$. Semi-volatile species compose a fraction of the organic carbon which exists in the atmosphere in an equilibrium between particle and gas phases. This equilibrium depends on temperature, vapor pressures of individual species, and the amounts and types of adsorbing particle surfaces. The amount of these species in the particulate phase collected on the filter depends on sampling conditions (e.g., filter face velocity). In this guidance, semi-volatile carbon is defined as that collected on pre-filter denuders and sorbent traps placed downstream of the collection filter on conventional samplers. At present the differentiation of C_o from C_e and C_c from C_e are method dependent. In spite of the limitations, the first and fundamental step of carbon speciation is the

semi-quantitative assessment of C_o , C_e and C_t from a quartz filter analyzed by thermal optical analysis (NIOSH 5040).

Organic compounds can represent a large fraction of fine particle mass. Organic compound speciation can provide a great deal of information regarding the sources and formation processes of carbonaceous particles. Identification of individual organic compounds is the subject of many ongoing research efforts, yet this goal is beyond the scope of the speciation program. Similarly, promising approaches for reduction of artifacts due to sampling of semi-volatile compounds are not yet ready for routine deployment; however, research directions suggest that current and future technological developments will permit both extensive quantification of individual compounds and accurate differentiation of semi-volatile gas and particulate phase organic carbon. Therefore, speciation of individual organics and accurate differentiation of semi-volatile species from C_t is optional. Although organic speciation is desirable, it is not simple to perform because there is no single analytical method that can be used to analyze all classes of organics. It may be more cost-effective to develop inexpensive methods that allow for the measurement of specific characteristic groups of organic compounds. Similar “lumping” approaches have been used successfully in ozone modeling. Attempting to obtain comprehensive spatial and temporal patterns for hundreds of organic compounds is not a cost-effective strategy.

Some species can be analyzed from more than one media and using other analytical instrumental methods. For example, PTFE filters can be extracted and analyzed for many of the same analytes as the quartz media. Also, inductively-coupled argon plasma (ICP) spectroscopy can be used to determine several trace metals, but the method is a destructive method of analysis and requires complete digestion of the filter sample. For consistency, the EPA will prescribe the use of the filter media, target species, and analytical methods identified in Table 3-1 for the 54 NAMS sites. If different target species, filter types and methods are used throughout the other 250 sites, implementation of an augmented quality control program with equivalency determinations is necessary in order to validate and evaluate the data for comparability.

4.0 NETWORK DESIGN

This section provides the recommended sites selected for the NAMS speciation network in Table 4-1, as well as outlines the general concepts to be applied when planning a PM_{2.5} network outside the scope of the core NAMS speciation sites. It also important to emphasize the need for integration of field and laboratory operations at the very early stages of program design. For example, the analytical laboratory personnel should be involved in target species selection and sampler procurement or design to ensure compatibility among sampling and analysis methods, filter media, and practical quantifiable limits. A representative flow diagram of the steps involved in network design is shown in Figure 4-1, while Table 4-2 in Section 4.4 contains an example outline of typical components to incorporate in a program plan. Such a plan is essential for ensuring that all participants understand the roles and responsibilities defined for the program.

The network of stations should be designed to meet the monitoring program objectives. At a minimum, the elements outlined below should be addressed in designing a chemical speciation network and developing a program plan. For additional information on the concepts of network design, methodology for developing planning areas, selecting and evaluating monitoring sites, and usage of existing resources for network design refer to *Guidance for Network Design and Optimum Site Exposure for PM_{2.5} and PM₁₀*, (U.S. EPA, 1997a). This reference contains information that builds upon the guidance specified for PM₁₀ monitoring associated with the previous NAAQS.

4.1 Establish Monitoring Objectives

The first step in network design is to determine the overall monitoring program goals and objectives and subsequent data quality objectives. General characterization of the atmospheric aerosol, air quality trends analysis, source attribution, and control strategy development and evaluation are primary objectives of the PM_{2.5} speciation monitoring program. The PM_{2.5} monitoring networks producing mass concentrations for attainment determinations do not provide samples amenable to chemical analyses for all species due to the limitations of a single-filter media. Source attribution, control strategy development, and aerosol characterization require chemical speciation; therefore, additional measures must be taken to address these objectives. In addition, data from the speciation monitoring networks may be augmented for determination of metals, organics, and particle morphology for non-routine NAMS in order to meet specified data use objectives.

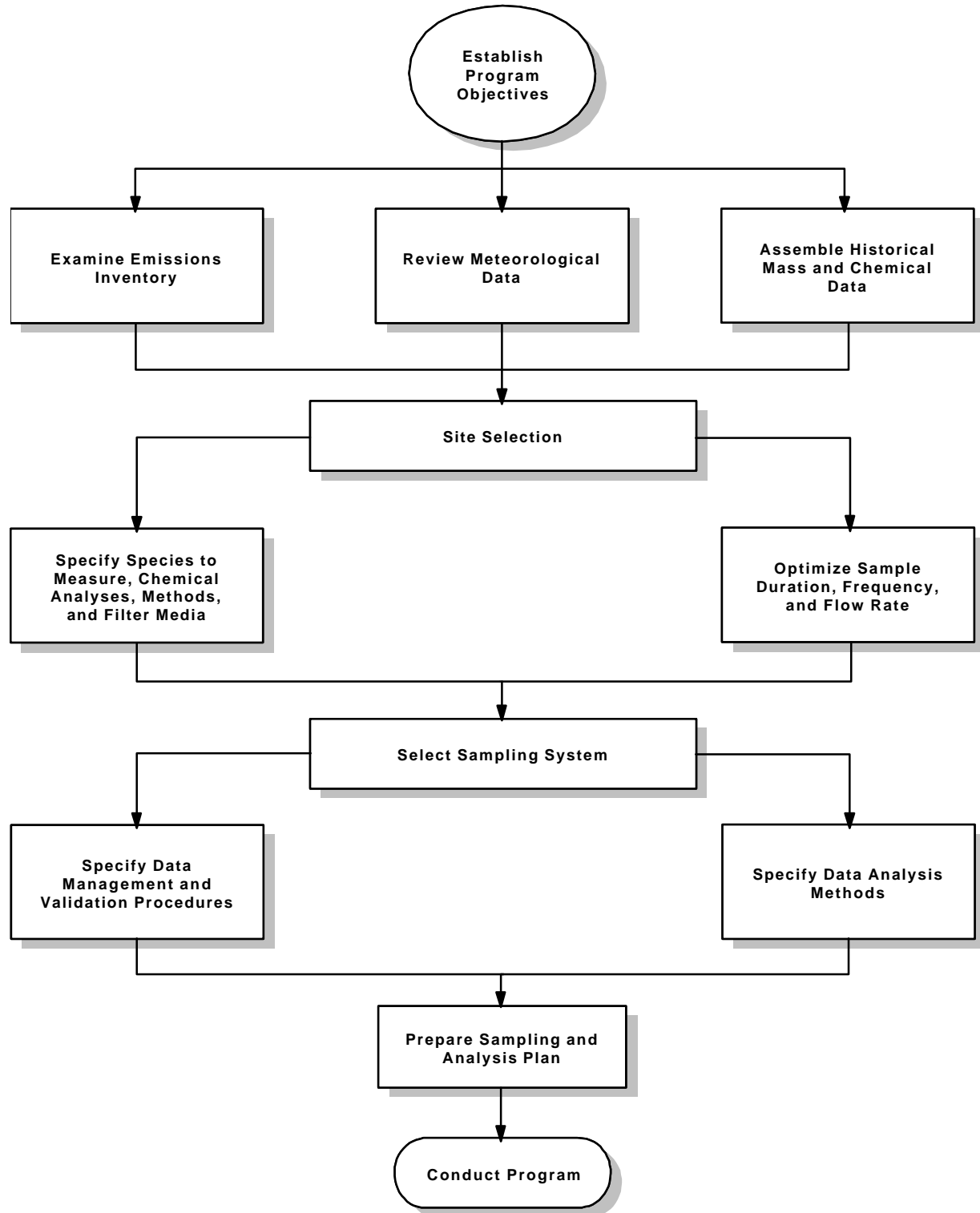


Figure 4-1. Network design flow diagram

4.2 Site Selection

Site selection is an important task in the design of a monitoring network and must result in the most representative sampling locations with characteristics that match the monitoring objectives. Proper siting requires precise specification of the monitoring objectives which usually includes a desired spatial scale of representativeness. Information from emissions inventories, meteorology data, and available historical mass and chemical data are used to determine candidate locations for sampling. This information is used in conjunction with the program objectives to determine the appropriate site selection. Specific criteria to be used in siting the NAMS monitoring stations, including spacing from roadways and vertical and horizontal probe placement can be found in Appendix E of CFR Part 58 (62 FR 38763).

Appendix D of the Part 58 PM_{2.5} Regulations (62 FR 38763) provides general criteria applied in establishing networks and for choosing general locations for new monitoring stations for PM_{2.5}. The general requirements for chemical speciation include a national network of approximately 50 sites to include approximately 25 PM_{2.5} core sites collocated at PAMS sites (1 type 2 site per PAMS area). Selection of the remaining was based on recommendations from EPA with review and feedback from State and local agencies.

PAMS type 2 sites were established as maximum ozone precursor emission impact sites. These sites were established to monitor the magnitude and type of precursor emissions in the area where maximum precursor emissions representative of a MSA/CMSA are expected to impact and are suited for monitoring urban air toxic pollutants. Generally, the type 2 sites are located immediately downwind of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district or primary area of precursor emissions mix to obtain neighborhood scale measurements.

Monitoring and sampling parameters are generally consistent among PAMS type 2 sites. For most sites, an intensive sampling period takes place during the summer (typically June-August) while a reduced set of measurements are made less-frequently during the remainder of the year. During the intensive summer period, the following sampling and monitoring parameters and minimum monitoring frequencies are measured at PAMS:

- ▶ Volatile organic compounds (VOCs) - Eight 3-hr samples daily, hourly automated measurements are typically taken at the Type 2 sites, and one 24-hour sample every 6th day year round;
- ▶ Carbonyls - Eight 3-hr samples daily, one 24-hour sample every 6th day year round;
- ▶ Ozone - Continuous sampling; and

- ▶ NO/NO₂/NO_x or NO/NO_y - Continuous sampling.

In addition to VOC, carbonyl, O₃ and NO_x pollutant parameters, each type 2 site is equipped with a ten meter meteorological tower to provide surface meteorology for wind speed and direction, temperature and humidity. Each site also has access to area upper air data and surface measurement of barometric pressure, precipitation, and solar/UV radiation. Therefore, collocation of selected PM_{2.5} speciation trends sites with PAMS type 2 sites offers some benefits with respect to having the ability to accumulate long-term data on organic compounds, particulate nitrate precursors, and local meteorology in conjunction with PM_{2.5} mass and chemical composition data. In most cases, the existing site platforms are rugged and capable of incorporating a modest amount of additional sampling equipment. It is necessary to locate a PM_{2.5} Federal Reference Method sampler at the PAMS site in addition to the speciation sampler to provide a basis for long-term comparison of particulate mass and chemical constituents.

Table 4-1 lists the recommendations for location of the 54 sites to be used to implement the speciation trends network. The current recommendation includes 20 PAMS sites and 34 other sites either identified by AIRS location or MSA. The selection of MSAs, as well as PAMS cities, was based on a balance of several factors, including:

- ▶ Location of existing PAMS and IMPROVE sites;
- ▶ Geographic location of MSAs using 1996 population statistics;
- ▶ Ozone non-attainment areas; and
- ▶ PM₁₀ non-attainment areas.

The locations of existing PAMS and IMPROVE sites generally leave a large portion of the Central, Midwestern, and Southeastern US void of monitoring data that could be used for trends purposes. Therefore, we have balanced our recommendations for trends sites to specifically include major population areas in these regions which, in many cases, also include areas of higher PM_{2.5} primary and precursor emissions within the region. The map given in Figure 4-2 illustrates the overall geographical coverage of the recommended speciation trends network. The IMPROVE program will also expand its total number of sites and preliminary information indicates that additional sites will be located in the Great Plains area and in New Mexico. This will further complement the integration of the IMPROVE and PM_{2.5} chemical speciation network. In locating the speciation site within each of the suggested MSAs, it is suggested that a community-oriented PM_{2.5} core site expecting the maximum concentrations be selected as the speciation trends site. Also, it is desirable to outfit each of the 34 MSA sites selected with a ten meter meteorological tower for collecting data on wind direction and speed, temperature, and humidity. Local siting limitations and/or unique spatial and temporal variabilities of PM_{2.5} may

require some balance and adjustment of the criteria outlined above to determine final site selection.

4.2.1 Target Species and Sampling Frequency and Duration

For the non-routine NAMS, the next step is to determine which chemical species beyond those specified for the routine program, are to be measured and at what concentrations they are expected to be present in the ambient air. It is imperative to include those target species required to meet the data use objectives. For example, if source attribution is an objective, it may be desirable to measure species which are present in, or indicative of, the sources which are suspected of contributing to the PM_{2.5} mass.

Potential source contributions can often be determined from emissions inventory summaries in the study area. These inventories should include emissions factors for suspended particles, CO, SO₂, NO_x, VOC, and NH₃, if possible. The gaseous precursors are needed to assess whether or not secondary aerosol might contribute to elevated PM_{2.5} concentrations. Some inventories may contain additional information such as the elemental or organic composition of the particulate emissions and estimates of their particle size distribution. These data, if available, are valuable in selecting sampling site locations and developing a sampling plan to consider target analytes important in a particular location.

When gridded inventories are available, or the locations of point sources are known, these should be examined to determine the locations of emissions relative to sampling locations. The closer the source, the greater the probability that some of the chemicals emitted will be detected at the receptor. Unusual or exceptional events should be identified, such as prescribed fires, wildfires, construction and demolition activities, and plant upsets. These may have a different chemical character from the sources which are listed in the inventory. Agricultural extension offices should be contacted to obtain land-use maps and soil conservation surveys. Periods of tilling, fertilizing, and grazing might be indicative of elevated emissions from these activities. Local fire departments, the National Forest Service, the Bureau of Land Management, and other fire management agencies can often supply information on local burning events.

Micro inventories are also helpful for identifying potential contributors and the chemical species which correspond to these contributions. Micro inventories include detailed surveys and locations of vacant lots, storage piles, major highways, construction sites, and industrial operations. These are plotted on a map with notes regarding the visual appearance of each potential emitter. For example, if chimneys are present in a residential neighborhood, this observation is recorded and photographs are taken. Roads in the vicinity of sampling sites are

classified with respect to the type of traffic on them and whether or not they have sidewalks and paved shoulders.

Expected emissions cycles should be examined to determine sampling periods and durations. For example, residential wood burning will usually show up on samples taken during the night, whereas agricultural burning will usually show up during the daytime. While these two source types may be indistinguishable based on their chemical profiles, their diurnal cycles will provide convincing evidence that one or the other is a major contributor when both activities occur simultaneously. If local, cyclical emissions are occurring, variable sampling times (e.g., 24-hr vs. day/night 12-hr cycles) may be important in understanding the contribution of local emissions to measured PM_{2.5} concentrations. The timing of other events, such as major prescribed burning or accidental wildfires, may be more difficult to predict.

Particle size is of value in separating one source from another. Particle size fractions, chemical analyses, sampling frequencies, and sample durations need to be considered because more frequent samples, or samples taken at remote locations, may require a sequential sampling feature to minimize operator costs. Shorter sample durations may require a larger flow rate to obtain an adequate sample deposit for analysis. The types of analyses and size fractions desired affect the number of sampling ports and different types of filter media needed.

Calculate the expected amount of deposit on each filter for each chemical species and compare it to typical detection limits for the analyses being considered. Urban samples acquire adequate deposits for analysis with flow rates as low as ~20 L/min for as short as 4-hour sample durations. Samples at nonurban sites may require >100 L/min flow rates for 24-hour durations to obtain an adequate deposit for chemical speciation. However, sampler flow rates as well as filter surface areas also have effects on the collection efficiency of certain target analytes.

4.3 Sampling System Selection

Select a sampling system which provides the most cost-effective and reliable means of meeting the monitoring needs. In complicated situations, especially those with many contributing sources, unknown sources, or secondary contributions, more complex sampling systems are needed. Both reference and research sampling systems have been operated side-by-side in many PM₁₀ studies when this is the case, and the same practice can be applied to PM_{2.5} monitoring. Refer to Section 6.0 for a discussion of the sampling methodology and candidate speciation sampler approaches for the core NAMS network.

Table 4-1
Proposed Sites for the PM_{2.5} NAMS Trends Network

Region	State / Common.	MSA/Site	PAMS City Site	AIRS #
1	Connecticut		East Hartford	09-003-1003
	Maine		Kittery	23-031-3002
	Massachusetts		Lynn	25-009-2006
	Massachusetts		Chicopee	25-013-0008
	Rhode Island		East Providence	44-007-1010
	Vermont	Burlington		
2	New York		Bronx Gardens	36-005-0083
		Rochester		
	New Jersey ¹		New Brunswick	34-023-0011
	Puerto Rico	San Juan		
3	Washington DC		McMillan Reservoir	11-001-0043
	Maryland		Essex	24-005-3001
	Pennsylvania		E. Lycoming	42-101-0004
		Pittsburgh		
	Virginia	Norfolk		
4	Alabama	Birmingham		
	Florida	Miami		
		Tampa		
	Georgia		S. Dekalb	13-089-0002
	Mississippi	Biloxi		
	North Carolina	Charlotte		
	South Carolina	Charleston		
	Tennessee	Memphis		
5	Illinois ¹		Chicago-Jardine	17-031-0072
	Indiana	Indianapolis		
	Michigan	Detroit		
	Minnesota	Minneapolis		
	Ohio	Cleveland		
	Wisconsin		Milwaukee	55-079-0041

Region	State / Common.	MSA/Site	PAMS City Site	AIRS #
6	Louisiana		Capitol	22-033-0009
	Oklahoma	Tulsa		
	Texas ¹		Clinton Dr.	48-201-1035
			Hinton	48-113-0069
			Chamizal	48-141-0044
7	Kansas	Kansas City		
	Missouri	St. Louis		
	Nebraska	Omaha		
8	Colorado	Denver ¹		
	Montana	Great Falls		
	North Dakota	Grand Forks		
	Utah	Salt Lake City		
9	Arizona	Phoenix		
	California	Los Angeles		06-037-1103
		Riverside (Rubidoux) ¹		06-065-8001
			El Cajon	06-073-0003
			Simi Valley	06-111-2002
			Sacramento	06-067-0006
		Bakersfield		06-029-0014
		Fresno		06-019-0008
		San Jose		06-085-0004
	Nevada	Reno		
10	Idaho	Boise		
	Oregon	Portland		
	Washington	Seattle ¹		
Network Totals	39 States	34 MSAs/Sites	20 PAMS Sites	54 Trends Sites

¹ Selected as co-located speciation sampling sites.

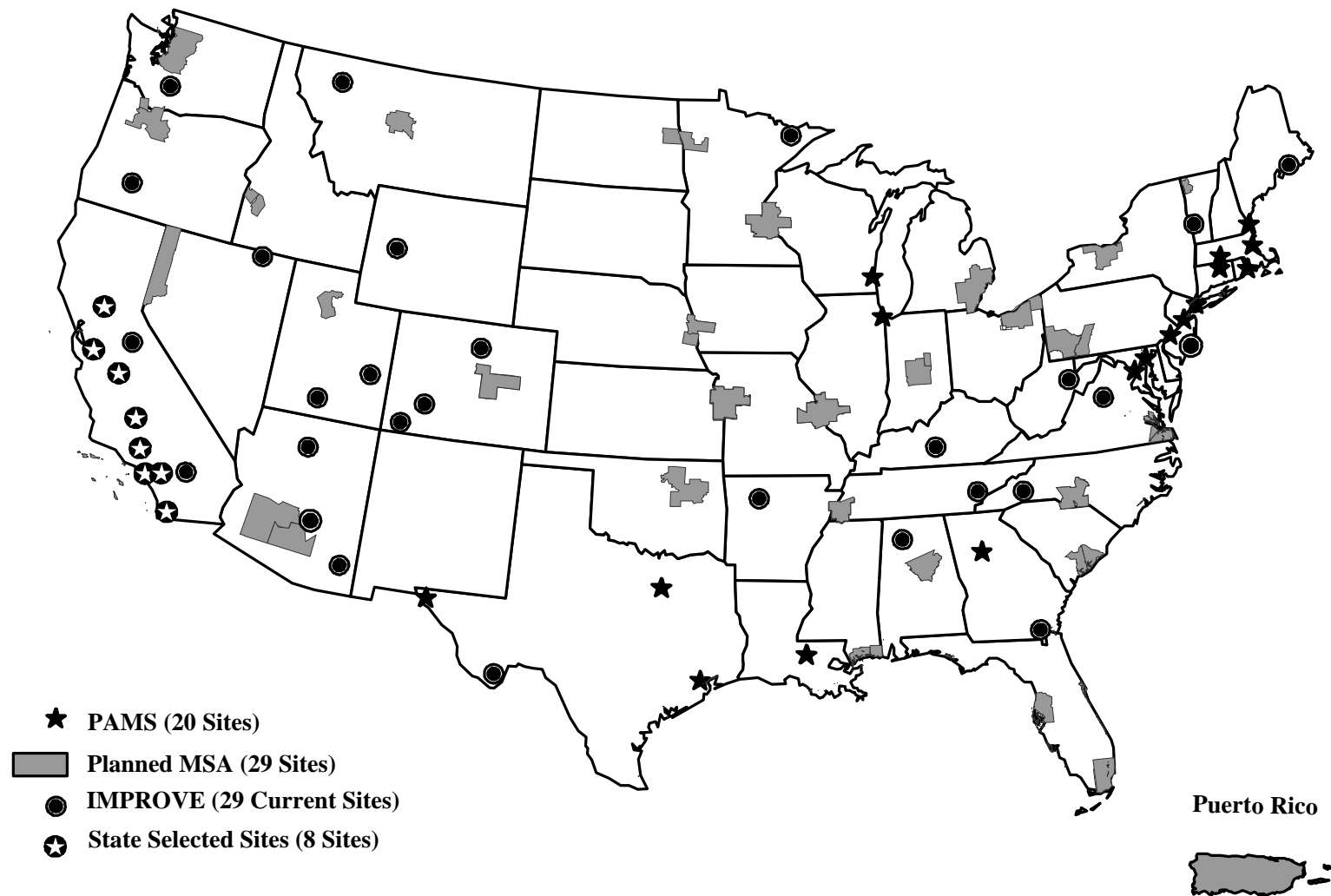


Figure 4-1. Proposed speciation trends sites and current IMPROVE sites.

4.4 Speciation Sampling and Analysis Plan Preparation

The final step is to create a written sampling and analysis plan. The plan specifies the study objectives, sampling locations, analysis methods, filter media, sampling systems, sampling frequencies and durations. Details should be included which prescribe nominal flow rates, methods and schedules for inlet cleaning, calibration and performance tests, filter transport and handling procedures, database management system, data analysis methods, and record keeping protocols. An example of an outline of the contents for a program plan is given in Table 4-2.

Table 4-2
Example of Program Plan Outline for PM_{2.5} Measurements

<p>1.0 INTRODUCTION</p> <p>1.1 Background</p> <p>1.2 Objectives</p> <p>1.3 Overview</p> <p>2.0 AIR QUALITY IN THE STUDY AREA</p> <p>2.1 Emissions</p> <p>2.2 Meteorology</p> <p>2.3 Atmospheric Transformations</p> <p>2.4 Historical Air Quality Data</p> <p>2.5 Implications for PM_{2.5} Study Design</p> <p>3.0 DATA ANALYSIS AND MODELING</p> <p>3.1 Data Evaluation</p> <p>3.2 Descriptive Air Quality Analysis</p> <p>3.3 Descriptive Meteorological Analysis</p> <p>3.4 Source Profile Compilation</p> <p>3.5 Emissions Inventory</p> <p>3.6 Receptor Model Source Apportionments</p> <p>3.7 Trajectory Modeling</p> <p>3.8 Secondary Aerosol Modeling</p> <p>3.9 Case Study Descriptions</p> <p>4.0 PROPOSED AMBIENT MONITORING NETWORK</p> <p>4.1 Sampling Sites</p> <p>4.2 Sampling Frequency and Duration</p> <p>4.3 Sampling Methods</p> <p>5.0 EMISSIONS CHARACTERIZATION</p> <p>5.1 Emissions Activities and Micro inventories</p> <p>5.2 Geological Source Profiles</p> <p>5.3 Motor Vehicle Exhaust Characterization</p> <p>5.4 Residential Wood Combustion Characterization</p> <p>5.5 Industrial Source Emission Characterization</p> <p>5.6 Other Source Characterization</p>	<p>6.0 LABORATORY OPERATIONS</p> <p>6.1 Substrate Preparation</p> <p>6.2 Gravimetric Analysis</p> <p>6.3 Light Absorption</p> <p>6.4 Elemental Analysis</p> <p>6.5 Filter Extraction</p> <p>6.6 Ion Analysis</p> <p>6.7 Carbon Analysis</p> <p>6.8 Specialized Analysis</p> <p>7.0 QUALITY ASSURANCE</p> <p>7.1 Standard Operating Procedures</p> <p>7.2 Quality Audits</p> <p>7.3 Standard Traceability</p> <p>7.4 Performance Tests</p> <p>8.0 DATA PROCESSING, DATA BASE MANAGEMENT, AND CHAIN-OF-CUSTODY</p> <p>8.1 Data Base Requirements</p> <p>8.2 Levels of Data Validation</p> <p>8.3 Continuous Data Processing</p> <p>8.4 Substrate Data Processing</p> <p>9.0 MANAGEMENT, REPORTING, AND SCHEDULE</p> <p>9.1 Tasks and Responsibilities</p> <p>9.2 Resource Requirements</p> <p>9.3 Reports</p> <p>9.4 Schedule and Milestones</p> <p>10.0 REFERENCES</p>
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5.0 SAMPLING ARTIFACTS, INTERFERENCES, AND LIMITATIONS

This section discusses some of the general difficulties that may be encountered while making aerosol measurements. Particle and gas removal by inlets, nitrate particle volatilization, adsorption of SO₂ and NO_x, organic carbon adsorption and volatilization, liquid water content, electrostatic charge, and passive deposition and recirculation are discussed. Some of these biases can be avoided or counteracted with alternative sampling and filter handling techniques.

5.1 Inlet Surface Deposition

The materials from which inlets are manufactured can affect the collected aerosol, especially when gas and particle phases are being quantified for volatile species such as ammonium nitrate. Most samplers are manufactured from aluminum, plastic, or galvanized steel, due to availability and economy. These materials can absorb some gases, especially nitric acid, and can change the equilibrium between volatile particles on a filter and the surrounding air.

Nitric acid has a tendency to adhere to surfaces. Surfaces coated with perfluoroalkoxy (PFA) Teflon® can pass nitric acid with 80 percent to 100 percent efficiency. Aluminum surfaces common to many samplers and inlets have a large capacity (60-70 percent) for absorbing nitric acid vapor while transmitting particles with high efficiency. If measurement of nitric acid is important to the non-routine NAMS component of the speciation program, then coating of the inlet is necessary. Denuders are often used as part of, or located immediately behind, size-selective inlets to remove gases that might interfere with the aerosol measurement. See Section 5.2.2 for a more detailed discussion of denuders.

Plastic surfaces can acquire an electrical “static” charge which might attract suspended particles, although the dimensions of most ambient sampling system inlets are sufficiently large that the attraction is negligible.

5.2 Nitrate Particle Volatilization

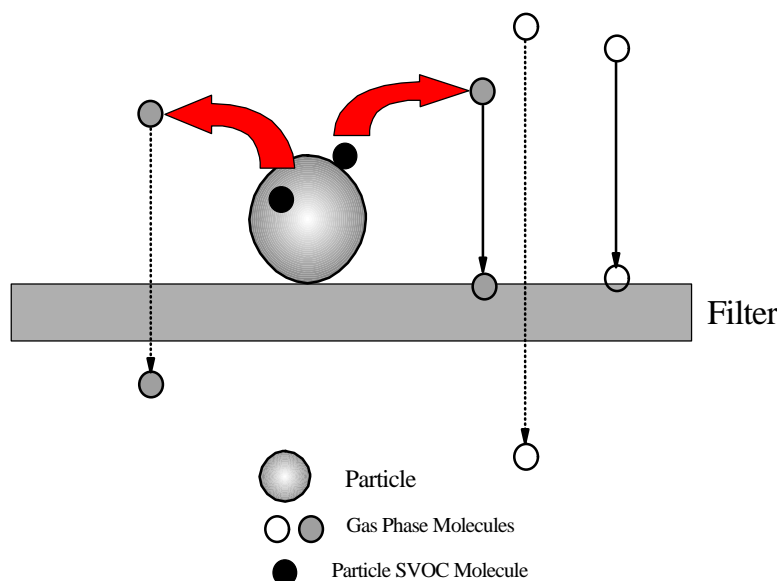
Nitrate losses during and after sampling have been reported. At temperatures greater than 30 °C, most nitrate will be in the gas phase as nitric acid (HNO₃), while at temperatures lower than 15 °C, most nitrate will be in the particle phase as ammonium nitrate (NH₄NO₃). There will be varying amounts of nitric acid and ammonium nitrate at the intermediate temperatures. Relative humidity and concentrations of ammonia and nitric acid gases also affect this equilibrium, but temperature is by far the most important variable. When air temperature changes during sampling, some of the ammonium nitrate already collected on the filter can volatilize. Nitrate

volatilization is minimized when ambient temperatures are low and with proper ventilation of the sampler housing.

Volatile compounds can also leave the filter after sampling and prior to filter weighing or chemical analysis. Losses of nitrate, ammonium, and chloride from glass and quartz-fiber filters that were stored in unsealed containers at ambient air temperatures for 2 to 4 weeks prior to analysis exceeded 50 percent (Witz et al. 1990). Storing filters in sealed containers and under refrigeration will minimize these losses.

5.3 Organic Carbon Volatilization

The collection and determination of particulate organic material is complicated by changes in equilibrium between organic material in the gas and particulate phases during sample collection. Volatilization of individual semi-volatile organic species depends on both temperature and filter face velocity due to flow rate. Gas phase organic molecules in the sample stream or on the



particulate matter may either be adsorbed by the quartz filter or pass through the filter during sampling (Figure 5-1). If corrections are not made for collection of gas phase components by the quartz filter, the amount of carbonaceous material determined from the analysis of the filter for carbon may result in a positive bias (Cui et al., 1997). Also, a larger negative error results from the loss of 20-80 percent of the particulate phase organic material during sampling (Eatough et al., 1993).

Figure 5-1. Artifacts associated with collection of particulate carbonaceous material (Adapted from Cui et al. 1997)

Volatilization of organic carbon is typically addressed by sampling with two quartz filters in series and correcting the carbon found on the first filter by the amount of carbonaceous material found on the second filter (Eatough et al., 1995, Appel et al., 1989, McDow et al., 1990).

However, it is difficult to distinguish between the gas phase organic compounds collected on the particulate filter and the backup filter.

In addition to collection of gas phase organics by the particle collecting filter, particulate semi-volatile organic compounds (SVOCs) can volatilize from the collected particles during sampling (Cui et al., 1997). These SVOCs can be absorbed by the filter or pass through the filter and be lost (Figure 5-1). If only a fraction of the SVOCs which can be adsorbed by the quartz filter is adsorbed by the first filter, then the second filter may contain either gas phase organic compounds, SVOC lost from particles and subsequently adsorbed, or both (Eatough et al., 1995).

The capability for determination of semi-volatile organic aerosols will be added to the routine speciation program as the technology further develops and is validated for routine use. The approach to be used for the routine NAMS speciation program to correct for these artifacts during the collection of particulate organic carbon, is to incorporate the use of a diffusion denuder to remove the gas phase organic compounds (including volatile organic and semi-volatile organic compounds) prior to the collection of particles on a single quartz filter. A post-filter sorbent material like XAD-4 will also be necessary to collect the gas phase semi-volatile organic compounds volatilized from the particulate and the filter medium. The candidate speciation samplers have been designed to accommodate the necessary components as they are developed.

If the determination of semi-volatile organics is required to fulfill the objectives of the non-routine NAMS network, the analysis of the gas-phase semi-volatile organics collected by the denuder, in addition to the quartz filter and post-filter sorbent will be necessary. However, determination of semi-volatile organic aerosols is considered non-routine and research oriented in nature as discussed in Section 2.1.

5.4 Sample Moisture

The importance of liquid water content in ambient aerosol is recognized. As ambient relative humidity exceeds 70 percent, particle growth due to accumulation of moisture becomes significant. Theoretical calculation or experimental measurement of aerosol liquid content is complicated because growth rates vary with aerosol composition, ambient relative humidity and surface tension.

The current PM_{2.5} NAAQS FRM for mass measurements requires filter equilibrium at a relative humidity between 30 and 40 percent prior to weighing. If samples are collected in a very humid environment where soluble particles tend to aggregate in liquid water molecules, and then are equilibrated in a laboratory environment where the relative humidity is controlled at 30

percent, a difference in mass concentrations may occur depending on particle and filter composition. When samples are collected in an environment rich in sulfuric acid or ammonium sulfate, this bias could be as high as 15 percent to 20 percent. Therefore, to minimize the effect of liquid water on measured particles, it is recommended that relative humidity equilibration ranges be kept at the low end of the 30 to 40 percent range for filter weighing.

5.5 Electrostatic Charge

One problem that occurs when using a microbalance for filter weighing is electrostatic charge. Electrostatic charge is also referred to as static, static electricity, static charge and triboelectric charge. Electrostatic charge is the accumulation of electrical charges on a nonconductive, dielectric surface such as the surface of a Teflon®-membrane or polycarbonate-membrane filter. Residual charge on a filter can produce an electrostatic interaction that induces non-gravimetric forces between the filter on the microbalance weighing pan, and the metal casing of the electrobalance, thereby biasing mass measurements. As electrostatic charges build up during the weighing session, the readout of the microbalance becomes increasingly unstable (e.g., noisy).

To minimize the static charge during gravimetric analysis, it is necessary to place a radioactive antistatic strip inside the microbalance chamber prior to weighing. It may also be necessary to pass each filter near, but not touching, the antistatic strip prior to weighing. The most commonly used low-level radioactive antistatic strips contain 500 picocuries of polonium-210 (Po²¹⁰). Polonium strips are commercially available and have a half-life of 138 days. Polonium strips neutralize electrostatic charges on items within an inch of the strip surface. Antistatic solutions can also be used to coat the interior and exterior nonmetallic surfaces of the weighing chamber. This coating increases surface conductivity and facilitates the draining of electrostatic charges from non-metallic surfaces to metallic surfaces.

Charge neutralization may take longer than 60 seconds for situations in which a high amount of charge has developed on collected particles due to their origin, or the particle loading on the filter is large. Electrostatic charge build up becomes greater when the air becomes drier. A 60-second charge neutralization may be sufficient in ambient indoor air conditioned to 37 percent relative humidity and 23 °C. Earth-grounded conductive mats should also be placed on the weighing table surface and beneath the analysts feet to reduce electrostatic charge buildup.

5.6 Passive Deposition

Passive deposition of windblown dust on the filter prior to, and following sampling, can positively bias PM measurements. This deposition is minimal and dependent on local conditions during the specific collection time. Bias due to deposition can be minimized by more frequent sample filter changing (i.e., reduce the passive deposition period), pre-loading filters in the laboratory, and transporting unexposed and exposed filter cassettes in covered cassette holders.

Recirculation of the sampling pump exhaust is not expected to have an effect on PM_{2.5} mass measurements. However, it can effect carbon and trace metal speciation measurements when pump and armature wear are entrained in the exhaust. This contamination can be minimized by filtering pump exhausts or ducting them away from nearby sampling inlets. Even though PM_{2.5} pumps may be adequately filtered, nearby high volume samplers for PM₁₀ or TSP can still affect the PM_{2.5} measurements and require filtration or ducting.

For sampling, it is recommended that field blanks be periodically placed in the sampling system, without air being drawn through them, to estimate the magnitude of passive deposition during the period of time that filters are exposed in the sampler (24 hours). A field blank should be collected for each filter medium used. These blanks may also be used as trip blanks to evaluate the level of contamination during transport. Since field blanks values are dependent on local conditions, it is not appropriate to perform blank correction. The results are used to demonstrate that the contribution of passive deposition was negligible under the normal conditions of sampling.

5.7 Contamination Due to Handling

In order to avoid measurement errors due to damaged filters or a gain or loss of collected particles on the filters, careful handling of the filter during sampling, transport, equilibration, and weighing is necessary. When filters are handled, the analyst should wear gloves that are antistatic and powder-free to act as an effective contamination barrier. Gloves that are packed in a box can carry an electrostatic charge and should be discharged by touching a good electrical ground after putting them on. The filters should be handled carefully by the support ring, if present, rather than the filter material using smooth, non-serrated forceps only for this purpose. It is a good idea to mark the forceps to distinguish them from forceps used for other purposes, such as handling mass reference standards. Forceps should be cleaned with alcohol and lint-free wipes before handling filters and then should be allowed to air dry. These precautions reduce the potential effect of body moisture or oils that may contact the filters and subsequently affecting the analytical results.

5.8 Filter Media Artifacts

It is important to utilize the appropriate denuder for acid gases while making particulate speciation measurements and to maintain the denuder for optimal efficiency while in use. A regular denuder replacement schedule must be incorporated into any PM_{2.5} speciation program. Sampling filters can collect gases as well as particles onto the surface, or onto the particles collected on the surface, constituting an artifact. This process may change the weight of the filter, causing artifacts that significantly alter the estimated concentration. Artifacts can be formed by oxidation of acid gases (e.g., SO₂, NO₂) or by retention of gaseous nitric acid on the surface of alkaline (e.g., glass fiber) or other filter types. The magnitude of the effect is dependent on the concentration of the gases and also affected by the sampling period, filter composition and pH, and relative humidity. The magnitude and significance of the artifact is variable and dependent on local conditions and can be minimized or eliminated by use of an acid gas denuder. However, if the denuder is not properly maintained or replaced on a regular preventative schedule, acid gas breakthrough and the potential for artifact formation may occur.

Conversion of SO₂ on nylon filters has been shown to be highly variable and dependent on sampling conditions (Chan et al., 1986). The extent of the conversion of SO₂ to sulfate on Nylasorb nylon filters was found to depend on both the concentration of SO₂ and the relative humidity. The conversion was higher at lower SO₂ concentrations. More recent work (Batterman 1997) done to test the sorption of SO₂ on various filter types has shown the artifact formation for Teflon and quartz fiber filters to be insignificant. This study also showed the change in mass concentrations due to SO₂ sorption on nylon filters at the secondary 3 hour SO₂ NAAQS of 0.5 ppm to be small. The study did not directly address the potential for bias of sulfate measurements and examined the sorption on only clean filters without the presence of particles. Other work has shown there to be no statistical difference in measured sulfate on nylon filters with and without a denuder (Ashbaugh 1998).

Nitrate lost from inert filters (e.g., Teflon®) by volatilization and reaction with acidic materials also presents the potential for negative artifacts as discussed in Section 5.2 above.

6.0 SAMPLING METHODOLOGY

This section describes the sampling methodology for use in the NAMS chemical speciation PM_{2.5} program. For the routine component of the program, specific guidance for sampler selection and operation is provided to ensure consistency across the network for comparison of spatial data and trends analyses. To allow flexibility for speciation sampling at non-routine NAMS sites, State and local agencies can tailor sampling methodologies to their individual program needs. However, these non-routine speciation sites will be subject to a balance between the competing need for national consistency and the flexibility needed to address regional and local issues.

The chemical speciation program involves both sampling and analysis components. The “National PM_{2.5} Sampler Procurement Contract” includes the provision for the purchase of over 300 speciation monitors, including accessories, for establishing the speciation monitoring network. In some cases, the speciation sampler design is flexible and can include additional filter collection media best-suited for the analysis of specific components. The 40 CFR Part 53 requirements for designation of reference and equivalent methods for PM_{2.5} do not require designations for speciation monitors (U.S. EPA, 1997f). However, it is imperative that all non-reference or equivalent methods incorporate particle inlets and size fractionators with equivalent particle size efficiency curves to the reference method for PM_{2.5}.

Desirable features of a speciation sampler include the following:

- ▶ The inlet cut-point and separation profile must be comparable to the WINS, FRM. A number of laboratory and field tests should be conducted to demonstrate that the fine particle mass collected by the speciation monitor and the FRM are in good agreement (for example, have a slope of 1 ± 0.1 and r^2 better than 0.90).
- ▶ The sampler should use proven denuder technology to obtain nitrate and anion/cation measurements. The nitric acid denuder should be tested for its capacity and efficiency as a function of exposure time and relative humidity. If it is proposed that a denuder will be used for more than one sampling day, it will be important to demonstrate the collection efficiency over time.
- ▶ The sampler should collect samples at a face velocity and sample volume similar to that of the FRM with 46.2-mm diameter filters.
- ▶ The sampler must be reliable, rugged, and employ field-proven monitoring approaches.

There are several samplers which employ multiple channels and the appropriate filter media for use by State and local agencies in implementing the PM_{2.5} routine NAMS speciation program. The samplers mainly differ by inlet design and approach to collection of particles less than 2.5µm. More recent designs include the capability to collect semi-volatile organic aerosol particles using diffusion denuders followed by quartz fiber filters and solid sorbent traps. Three candidate sampler designs described in Section 6.2 are being made available through the EPA's National PM_{2.5} Sampler Procurement Contract.

6.1 Sampler Intercomparison Study

Several different speciation sampler designs could be used in the overall sampling program. Therefore, studies are needed to collect data which show intercomparisons between the samplers relative to the performance of the FRM inlet, chemical species, and corresponding mass measurement. EPA's goal for the intercomparison study is to determine if there are differences between the three PM_{2.5} speciation samplers available under the EPA National Contract, other samplers historically used for PM_{2.5} and the FRM.

Development of chemical speciation samplers for the National PM Sampler Contract was based on performance, rather than design criteria. This has allowed innovation in the development of these samplers and resulted in development of three slightly different approaches for meeting the performance criteria. Also as a result of review by the Speciation Expert Panel, the recommendation was made for an intercomparison among the chemical speciation samplers. The intercomparison will also include other historically accepted samplers (e.g., the IMPROVE sampler) and the FRM. The chemical species to be determined during the intercomparison study include only a subset of those specified for the routine NAMS speciation program.

6.1.1 Study Objectives

The objective of the intercomparison study is to determine if there are differences among the three chemical speciation samplers and how these samplers compare relative to other historical samplers, and to the FRM. While the FRM is considered the "gold" standard for mass, there are no such standards for the chemical components of PM_{2.5}. Thus, this intercomparison can only establish the relative equivalence of the samplers to each other on a species-by-species basis. For semi-volatile species (those in dynamic equilibrium between the gas and particle phases), the FRM which uses a PTFE filter provides only a lower limit of these species on the expected mass loading, since there is potential for loss of nitrate and SVOCs from the inert PTFE filters. For stable species (e.g., sulfate), the FRM should provide an accurate estimate of the mass loading for those species. Historical chemical speciation samplers like the Versatile Air Pollution Sampler

(VAPS) developed under an EPA contract, the Caltech gray box sampler (Solomon et al., 1989), or the South Coast Air Quality Management District's PTEMP sampler (SCAQMD, 1996) should provide a less biased value for semi-volatile species and provide an additional set of samples for comparison.

6.1.2 Overview of the Intercomparison

Collecting atmospheric particulate matter using the FRM with PTFE filters can result in negative sampling artifacts associated with the collected sample. Potential artifacts include the loss of volatile species, such as ammonium nitrate and semi-volatile organic compounds. Use of other filter media may result in negative or positive sampling artifacts. The magnitude of these potential artifacts depends upon the atmospheric concentration of the species being affected, the temperature, relative humidity, and, other variables. The chemical speciation samplers have been designed to overcome these potential biases or artifacts by the use of denuders to remove gas phase species and reactive substrates to collect species volatilized from the inert filters collecting the aerosol. Therefore, to evaluate the performance of these chemical speciation samplers they must be able to properly determine the chemical components of PM_{2.5} under a variety of atmospheric conditions, each of which will place different stresses on the performance of the sampler designs. This can be accomplished by sampling at different locations throughout the country, since the composition of the atmospheric aerosol is not identical across the country. For example, some areas have high nitrate and low sulfate level, while others have relatively high sulfate and low nitrate. Still, other areas are dominated by aerosol rich in organic compounds derived from automobile exhaust, by organic aerosol derived from wood smoke combustion, or from by organic aerosol derived from natural biogenic emissions. Some areas of the country are highly influenced by crustal material. In actuality, several of these conditions exist simultaneously, with one or two components being higher than the others.

A variety of atmospheric chemical conditions also may be observed at one location during different seasons. For example, sulfate is likely highest in the east during the summer when photochemistry is high, while nitrate is highest in the west in the winter when cool temperatures drive the ammonium nitrate equilibrium with nitric acid and ammonia to the aerosol phase. Due to time constraints, the study will be conducted over about an eight week period at four different locations to obtain as wide a difference in chemical atmospheres as possible. These constraints, however, result in limitations and follow-on studies will have to occur to fully test the equivalency of these samplers. For example, by sampling in the winter in the east, we are missing the highest sulfate concentrations, we are not sampling at a site with high wood smoke emissions, and we are sampling in Phoenix for crustal material in the winter when highest concentrations are likely to be observed in the summer.

Due to time and resource limitations, the study design is being conducted in two phases, the latter phase dependent on additional available resources. Phase I will be centered on sampling in areas with the following atmospheric conditions: high sulfate and low nitrate, high nitrate and low sulfate, and high crustal material. A fourth site was chosen locally EPA's laboratories in Research Triangle Park to allow for a more thorough evaluation of the samplers and their in-field operational performance. Phase II will include collecting samples at other locations where PM_{2.5} aerosols are thought to contain significant levels of wood smoke or biogenic carbon, or at key locations during summer months to evaluate high sulfate or crustal component conditions.

The time schedule for Phase I of the study dictates that sampling occur more frequently than every 6th day, as the results are needed by OAQPS by early March for input into the decision process for choosing chemical speciation monitors for the NAMS network. Therefore, samples will be collected every-other-day. The statistical design requires a minimum of 10-15 samples. To ensure that a sufficient number of samples are collected to meet that objective, 16 sampling periods will be attempted with a contingency of four additional sampling periods for a total maximum of 20. Samples will be analyzed for the major chemical components using standard analytical techniques. Data analysis will provide a robust test of the similarity of the samplers studied and, within the limitations of the study, reasons for differences among the methods tested.

6.1.3 Study Design

The design of this program is constrained by time limitations and resources available to complete the program (e.g., number of samplers, personnel, and funding). However, the statistical design was prepared understanding these limitations and the design chosen will provide a robust evaluation of the samplers relative to each other, to several samplers used historically to obtain similar data, and to the FRM. A secondary objective of this study is to evaluate the operational performance or practicality of the samplers in the field, that is, reliability, ruggedness, ease of use, and maintenance requirements. There are two major scientific hypotheses to be addressed by this intercomparison study.

- ▶ One is associated with reconstructing the FRM mass.
- ▶ The second is associated with inter-comparing the concentrations from the various speciation samplers, which consist of two parts:
 1. The first part is associated with examining differences among the samplers, without regard to why there are differences, if they exist. This will be addressed through analysis of variance (ANOVA).

2. The second part will examine why there are differences, if they exist. Some are expected due to the different methods employed. This will be primarily addressed using the Student's t-Test.
- A third set of hypotheses is given dealing with the potential affect of different analytical methods on measured concentrations of the chemical components of PM_{2.5}. These include the effect of vacuum XRF or atmospheric pressure XRF on nitrate concentrations measured on PTFE filters and the effect of thermal optical reflectance (TOR) vs. thermal optical transmittance (TOT) on OC/EC concentrations.

The first two hypotheses are predicated on the assumption that the cut points for the samplers in this study are the essentially the same. This is a required assumption to address the following hypotheses. Also, it is important to establish the precision of the instruments and this will be done by collocating samples at one site. While this provides only a limited assessment of the precision, it will provide a first cut estimate of the precision for the statistical analysis to be performed here. If for example, the precision is estimated at 50%, then determining differences among samplers will not be as informative as if the precision were 10-15%. As a benchmark, the coefficient of variation for the differences in concentrations from collocated FRM instruments is required to be less than 10%, according to 40 CFR Part 58, Appendix A. Depending on the species, a range of precision from less than 10% to about 30% is anticipated (Solomon et al., 1998).

6.2 Available Candidate Sampling Approaches

The candidate sampling approaches to chemical speciation include the Reference Ambient Air Sampler (RAASTM), Mass Aerosol Speciation Sampler (MASS), Spiral Ambient Speciation Sampler (SASSTM) and IMPROVE. At a minimum, the speciation monitors used for these approaches contain PTFE, nylon, and quartz filter media and provide for the collection of the target analytes of interest. The PTFE filter will be used for mass and elements; quartz will be used for total, organic, elemental, carbonate carbon, and semi-volatile organic aerosols; and nylon will be used for the collection of nitrate and other cations and anions. The sampling system must also be capable of collecting a 24-hour PM_{2.5} sample. The candidate speciation monitor designs differ in their approach and are configured either as a multi-channel device operating from a single inlet, or a series of separate inlets or instruments, each with its own particulate separator mechanism. In any case, the monitor design must have the capability of collecting particles with an aerodynamic diameter equal to or less than 2.5 μm in a manner comparable to the FRM.

6.3 Operating Principle

The principle of operation involves several common components. Most fine particulate samplers have a size-separation device to separate particles so that only fine particles (those of approximately 2.5 microns) are collected onto the sample filter. Air is drawn through the sample filter at a controlled flow rate by a pump located downstream of the sample filter. The systems have two critical flow rate components for the capture of fine particulate: 1) the flow of air through the sampler must be at a flow rate to ensure that the size cut at 2.5 microns occurs; and 2) the flow rate must be optimized to capture the desired amount of particulate loading with respect to the analytical method detection limits. Other components such as a flow rate measurement device, denuder, temperature and barometric pressure probe and microprocessor control are also typical components of a speciation sampler. Key components of the candidate samplers for the speciation program are discussed below.

6.3.1 Particle Size Inlets

The inlet cut-point and separation profile must be comparable to the WINS, FRM inlet and be capable of removing particles which exceed the aerodynamic particle diameter of fine particulate matter. Size selective inlets typically use a variety of means to remove particles larger than the specified aerodynamic size and the size cutoff is based on sample flow rate. In the IMPROVE and RAAS, a cyclone is used. The SASSTM uses a spiral inlet and the MASS uses the PM_{2.5} FRM WINS assembly.

6.3.2 Denuder

Denuders are used immediately behind the size-selective inlet to remove gases that interfere with the aerosol measurements, or to quantify the concentrations of gases that are precursors to secondary aerosols. Denuders take advantage of the fact that gas molecules diffuse through air much more rapidly than small particles. Denuder surfaces are made of, or coated with substances that absorb the gases of interest while letting the particles pass through. Denuder geometries can be rectangular, cylindrical, honeycomb, or annular; the annular designs provide higher gas collection efficiencies than coated cylinders. The annular denuder design is well characterized for a wide range of applications involving acidic aerosols, ammonia, formaldehyde, and other chemical species. Honeycomb designs are composed of an array of narrow cylinders that combine high surface area with compact size. When the walls of the denuder are coated with substances that absorb the gases, the denuders may be washed and the extract submitted for special chemical analyses. This method is often used to measure nitric acid, sulfur dioxide, and

ammonia gases along with suspended particles. These gases are common precursors to secondary sulfate and nitrate compounds.

For the chemical speciation program, denuders are part of the sampler design primarily for the collection of nitrate on the nylon filter and organic carbon on the quartz filter. For removal of nitric acid, denuders coated with sodium carbonate or magnesium oxide will be used. For other applications, sodium carbonate denuders are also used to remove SO₂, HCl, HF, and HNO₂ from the air stream. For semi-volatile organics, technology for the routine removal of gas-phase semi-volatile organics has not been fully developed. The EPA and research community expect this capability to become available in the near future and employ the use of coated XAD-4 denuders. At this time, denuders will not be extracted and analyzed for vapor phase components as part of the routine NAMS.

Denuders have specific efficiencies and capacities depending on the design and coating materials used. It is recommended that acid gas denuders be recoated or replaced every 3 months, depending on the anticipated acid gas concentrations for each site or recommendations from the denuder manufacturer. For a detailed discussion regarding the use of annular denuder technology in the determination of acidic and basic gases (including sulfate, nitrate, and ammonium) of atmospheric fine particles refer to *Compendium Chapter 10-4* (U.S. EPA, 1997b).

6.3.3 Filter Types

Filter media include polytetrafluoroethylene (PTFE), quartz, and nylon. Other filter media types may be used in the non-routine NAMS component of the speciation network. Refer to Table 3-1 of this document for a matrix of filter types, target analytes and analytical methods used. Some physical and chemical characteristics of the filter media are given in Table 6-1. Also, Section 7 includes a brief discussion of the filter medium sample preparation procedures for lab analyses. Filter holders are expected to be made of an inert material. Since many of these materials are expected to be polymers, consideration should also be given to static electricity problems.

6.3.4 Flow Rate Measurement

Flow measurement and control for the speciation network are expected to be similar to the PM_{2.5} FRM requirements stated in 40 CFR, Appendix L to Part 50. The sampling system shall have a sample air flow rate control capable of providing a sample air volumetric flow rate, measured over intervals of not more than 5 minutes over a 24-hour period, that shall not vary

Table 6-1
Physical and Chemical Characteristics of Speciation Filter Media

Filter Type	Physical Characteristics	Chemical Characteristics
PTFE	Thin film of PTFE attached to ring without adhesive	Usually low blank levels
	White surface, nearly transparent	Made of carbon-based material, so inappropriate for carbon analysis
	Minimal diffusion or transmitted light	Inert to adsorption of gases
	High particle collection efficiency	Low hygroscopicity
	Cannot be accurately sectioned	Low blank weight
	Melts at approx. 60 °C	
	High flow resistance	
Nylon	Thin membrane of pure nylon	High HNO ₃ collection efficiency
	White opaque surface, diffuses transmitted light	Passively adsorbs low levels of NO, NO ₂ , PAN, and SO ₂
	Melts at approximately 60 °C	Low hygroscopicity
	High flow resistance	Low blank weight
Pure quartz-fiber	Mat of pure quartz fibers	Pre-washed during manufacturing
	White opaque surface, diffuses transmitted light	Low blank levels for ions
	High particle collection efficiency	Contains large and variable quantities of Al and Si; May contain other metals
	Soft, friable edges that have tendency to flake	Passively adsorbs organic vapors; Adsorbs little HNO ₃ , NO ₂ , and SO ₂
	Melts at >900 °C	Low hygroscopicity
	Moderate flow resistance	

more than ± 5 percent from the manufacturer's specified flow rate over the entire sampling period. Having tight control of sampler flow rate is a critical component of the speciation program since calculations of ambient air concentrations require knowing the volumetric flow rate through the sampler. Deviations from the expected flow rate that cannot be quantified reduce data quality.

6.3.5 Filter Temperature Measurement

Filter temperature measurement and control is an important element of the PM_{2.5} chemical speciation network. This is due to the characteristics of the aerosols that are being captured. If sampler performance resulted in significantly higher temperature at the sample media compared to the ambient temperature, then volatile chemical species may be underestimated. If filter media were colder than ambient temperature, as may be the case during a rapid temperature rise in the morning under conditions of a very low dew point, then more volatile chemical species may be trapped in the sample media than otherwise would occur under normal conditions. This would not necessarily invalidate data, however, it should be appropriately qualified. For these reasons, it is necessary for the sampler to provide a means to limit the temperature fluctuations and to monitor both ambient and filter media temperatures.

6.3.6 Barometric Pressure Measurement

The sampler must have the capability to measure barometric pressure and record the maximum, minimum, and mean measurements over the sampling period. The barometric pressure measurement is used for the purpose of computing the actual sample collection volume.

6.3.7 Relative Humidity Measurement

Particle growth due to accumulation of moisture is recognized in Section 5.4. When relative humidity is above 70%, particle growth due to accumulation may start to become significant. The capability for the sampler to measure ambient relative humidity is useful for input of this data into the overall data interpretation process.

6.4 Candidate Monitor Configurations for NAMS

The following is a description of candidate chemical speciation monitor configurations that may be used for both routine and non-routine NAMS sites. In addition, a very brief description of single channel, continuous, saturation and special purpose monitors also appropriate for use in

non-routine NAMS or special studies is provided. Table 6-2 provides a comparison of the sampler designs, filter types and target species analyzed.

Table 6-2
Target Analytes Associated with Filter Type and Sampler Design

Sampler Design	Teflon®	Nylon	Quartz
IMPROVE	Mass, elements	SO ₄ ⁼ , NO ₃ ⁻ , NH ₄ ⁺ , Na ⁺ , K ⁺	Carbonaceous aerosols
Met One SASS	Mass, elements	SO ₄ ⁼ , NO ₃ ⁻ , NH ₄ ⁺ , Na ⁺ , K ⁺	Carbonaceous aerosols
Andersen RAAS	Mass, elements	SO ₄ ⁼ , NO ₃ ⁻ , NH ₄ ⁺ , Na ⁺ , K ⁺	Carbonaceous aerosols
URG MASS400/MASS 450	Mass, elements, SO ₄ ⁼ , NO ₃ ⁻ , NH ₄ ⁺ , Na ⁺ , K ⁺	NO ₃ ⁻	Carbonaceous aerosols

6.4.1 IMPROVE

Each IMPROVE sampling module consists of an inlet stack; a cyclone to provide particle size cut based on flow rate; filter media for sample collection; a critical orifice that provides the proper flow rate for the desired size cutoff; a vacuum pump to produce the flow; and solenoids for exposing two filters. IMPROVE samplers consist of up to four parallel modules (three modules for PM_{2.5} and one for PM₁₀) and a common controller. A programmable clock, located in one of the filter modules or in a separate module, controls pump and solenoid switching for all filter modules. The pump(s) is housed separately. A schematic diagram of the IMPROVE sampler PM_{2.5} modules configuration is shown in Figure 6-1. Each of three modules utilizes a cyclone operating at a flow rate of 22.7 L/min to provide for a cut point of 2.5 μm.

One PM_{2.5} module uses a PTFE membrane filter to collect aerosols for mass measurement and subsequent analysis for trace elements. A second module is equipped with a sodium carbonate denuder and nylon filter to measure total particulate nitrate, anions and cations. The third module contains two pre-fired quartz-fiber filters in series to measure organic and elemental carbon on the first filter and to assess the extent of organic artifacts on the backup filter. The flow rate is monitored by two independent magnehelic gauges which measure pressure drop

across the cyclone and filter. A secondary measurement, using a pressure gauge behind the filter, provides a quality assurance check and ensures that the cassettes are properly seated. Flow control is maintained by a critical orifice between the filter and pump.

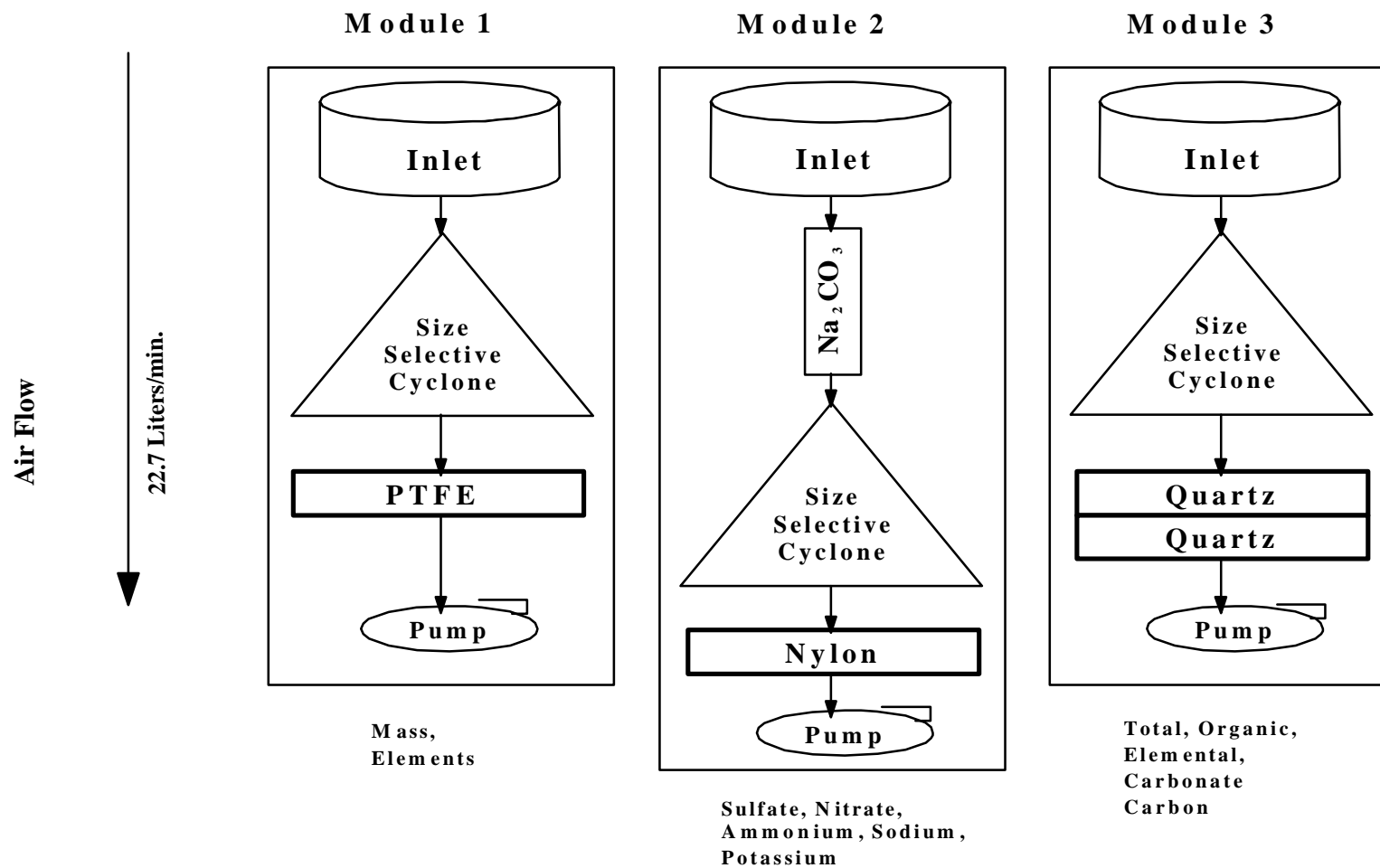


Figure 6-1. Schematic of the IMPROVE sampler modules.

IMPROVE samplers have historically been used at regional background and transport sites to fulfill SLAMS requirements. They were developed to quantify PM chemical components that affect visibility at Federal Class I areas that include national parks, national monuments, and wilderness areas.

6.4.2 Mass Aerosol Speciation Sampler (MASS)

The MASS consists of two stand-alone samplers. These samplers are identical except the MASS400 has a sodium carbonate coated denuder followed by a two stage Teflon® and nylon filter pack, while the MASS450 has a single stage quartz filter pack. On the MASS 400 the air stream travels through a sodium carbonate-coated denuder which removes HCl, HNO₂, HNO₃ and SO₂. The air stream then passes through a citric acid-coated denuder which removes NH₃. The remaining particulate passes through a 46.2-mm PTFE-filter which is analyzed for mass, elements, anions and cations. The PTFE filter is followed by a nylon filter which captures volatilized nitrate. The MASS 450 is designed for collection of carbon species. The MASS 450 may be retrofitted with a XAD-4 denuder and a PUF/XAD-4 sorbent trap to collect semi-volatile organic aerosols as the technology becomes available for routine application.

To obtain the fine particulate matter, the sample air inlet particle size separator is as specified in 40 CFR Part 50 Appendix L and identical to the FRM WINS. This provides an identical cut point and efficiency curve. These samplers use active volumetric flow rate control which is designed to meet FRM specifications and, therefore, has the same accuracy of flow as an FRM sampler. One modification of the inlet is a high capacity sodium carbonate annular denuder placed between the PM head and WINS inlet.

Perfluoroalkoxy (PFA) Teflon® coating of the inlet is an option that is available. This would allow particles and gases to pass through the inlet with high efficiency. If an accurate measurement of nitric acid is desired, then PFA-Teflon® coating is needed. Coated surfaces can pass nitric acid with 80 percent to 100 percent efficiency. Other materials, such as aluminum, can absorb some gases, particularly nitric acid, that may change the equilibrium between volatile particles on a filter and the surrounding air. Coating also minimizes oxidation of inlet internal and external surfaces, thus extending the life of the sampler.

The sampler configuration for both the MASS400 and MASS450 is shown in Figure 6-2. While an aluminum inlet will remove some of the nitric acid, it is not 100 percent efficient. Nitric acid is removed by using an annular denuder coated with sodium carbonate that quantitatively removes the acidic gases, including HNO₃, from the air stream. If NH₃

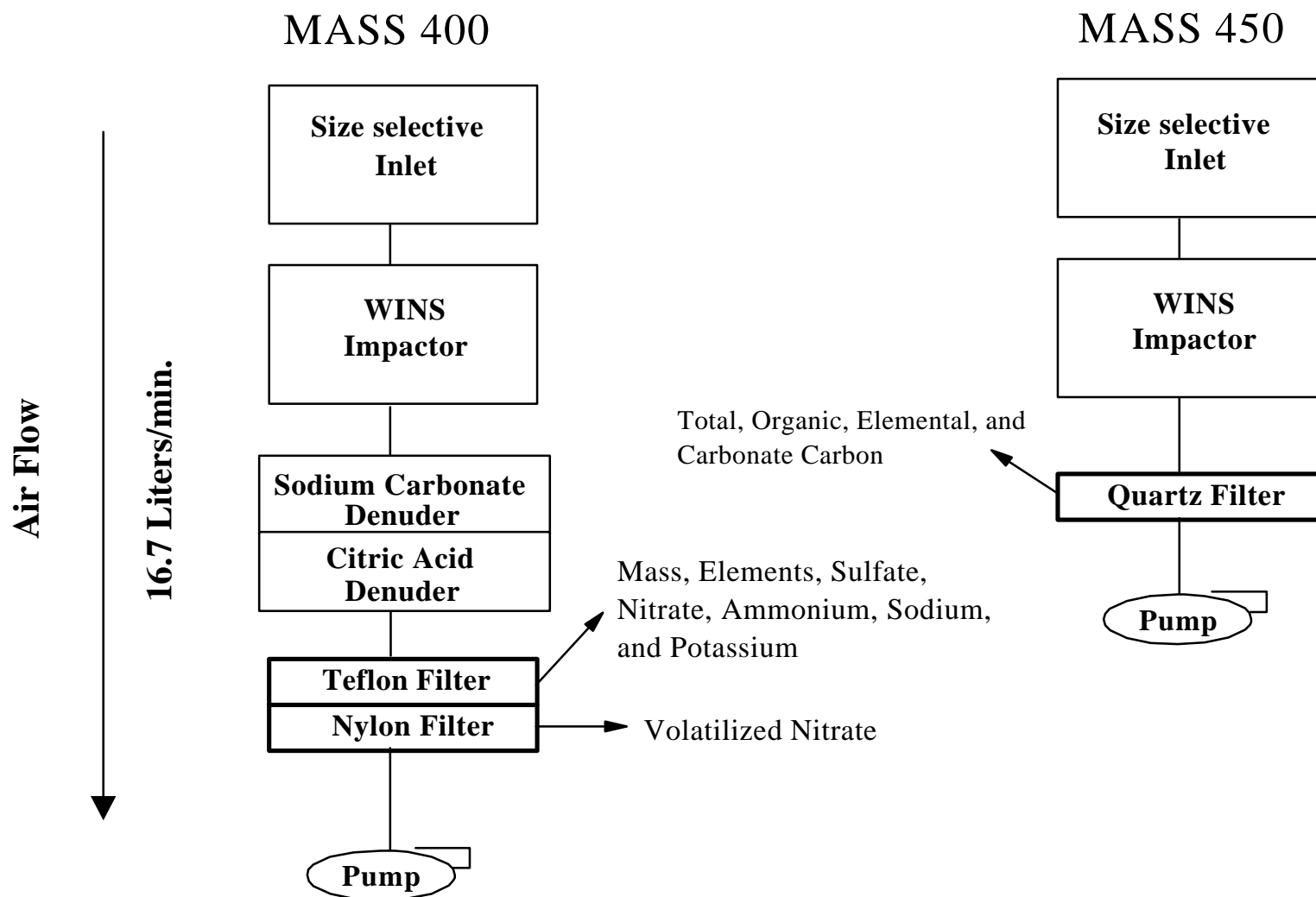


Figure 6-2. Schematic diagram of the MASS 400 and MASS 450 sampling systems

measurements are needed in conjunction with the aerosol measurement the denuder may be extracted and analyzed for ammonium ion content. In addition, if ammonia reacts with acid sulfates this effect, to differentiate between SVOC's in gas phase and the SVOC's that evaporate (negative artifacts) during sampling. Quartz filters have some affinity for gas phase SVOC's, thus, removing these species from the air stream minimizes their adsorption (positive artifact).

The PUF/XAD-4 trap will quantitatively collect the semi-volatile organic species that evaporate from the particles during collection of the sample. These organic species can be quantified by GC/FID/MS analysis of the XAD/PUF extracts or by evaporating the extract and weighing the residual materials. on the filter, a positive mass artifact would result.

6.4.3 Reference Ambient Air Sampler (RAAS™)

Ambient air is pulled through a wind direction and speed insensitive inlet and through an inert inlet line that is insulated from direct heating by the sun. The inlet has no size selective function. The air sample is directed via the sample downtube to a primary sample flow splitter into two streams. Each of the two flow streams in turn move through a AIHL-design cyclone separator which removes coarse particles with diameters larger than 2.5 μm . The cyclone requires a precise flow of 24 liters per minute to produce the correct cut point for sample collection. Following one side after splitting, the remaining particulate and gases are split again through the sample manifold into one, two or three outlet channels. The flow streams are then directed through the sample filters. The flow rate through each filter holder is controlled by a critical orifice that can be changed if a different sampler configuration flow rate is desired for special studies. The other half of the primary flow stream duplicates this flow path. A total of six channels are available for various speciation sampling objectives. For the routine chemical speciation program a total of 4 channels are used as shown in the schematic in Figure 6-3.

All inlet, manifold, connector and cyclone parts are fabricated from polytetrafluoroethylene (PTFE)-coated aluminum. Any combination of reactive annular denuders or filter materials can be attached with consideration for the flow requirements and species to be measured. In normal sampling, the combined flow rate to both filter holder assemblies is 24 liters per minute, which is divided into one 16.7 and one 7.3 liter per minute subdivisions. Two of these sampling lines collect fine particles on standard 46.2-mm diameter PTFE filters for subsequent chemical analysis. Two PTFE filters are used because samples intended for X-ray fluorescence analysis may be placed in a vacuum chamber during analysis leading to the expected loss of volatile aerosol components, thereby making it desirable to use a second PTFE filter for analysis for ionic species.

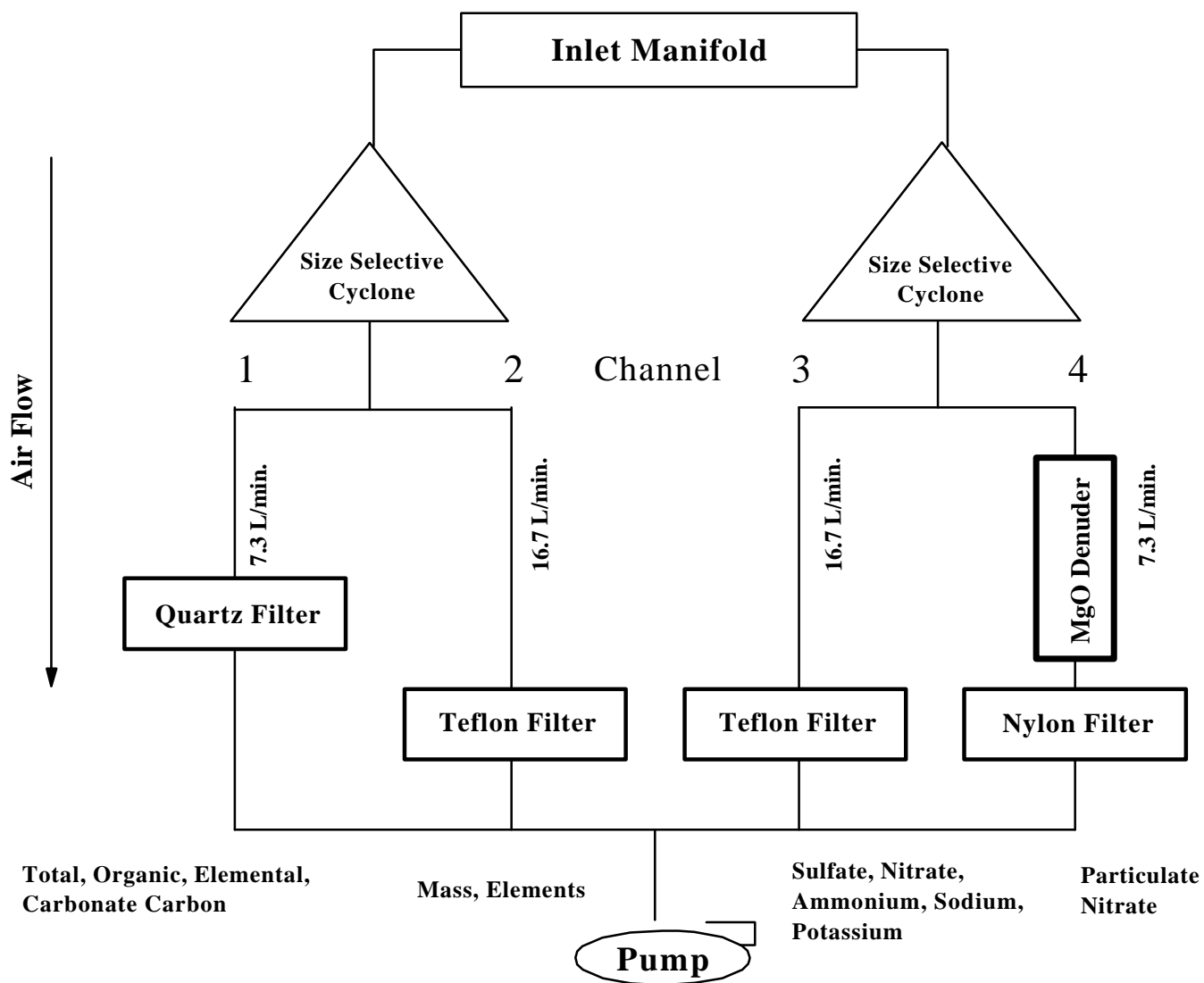


Figure 6-3. Schematic of the RAAS™ sampling system

A third filter holder is used to collect particles on a quartz fiber filter from which carbonaceous species can be measured by thermal optical analysis. If semi-volatile species are to be determined, a diffusion denuder coated with XAD to remove gaseous semi-volatile organics from the incoming air stream and a backup trap using polyurethane foam (PUF) or XAD resin to capture any semi-volatile organic components evaporating from the particulate captured on the filter may be used.

The fourth filter is a nylon filter located downstream from a magnesium oxide (MgO)-coated diffusion denuder. The diffusion denuder removes nitric acid vapor from the air stream while allowing fine particulate nitrate to pass through the denuder; then the nylon filter captures the fine particulate nitrate. The nylon filter is used because it has a high affinity for nitric acid. The nitrate content of any particulate ammonium nitrate (NH₄NO₃) that dissociates during sampling will be retained by the nylon filter. This system eliminates the well known negative sampling artifact for nitrates that can occur in locations such as Los Angeles and many cities in the West, that experience significant fine particle ammonium nitrate concentrations. A single denuded nylon filter is used rather than a nylon filter downstream from one of the PTFE filters to guard against the evaporative loss of ammonium nitrate (NH₄NO₃) from the PTFE filter after sampling has ceased but before samples are retrieved from the field. An optional PTFE-coated filter holder equipped with a nylon filter can be located in parallel with those filters that are directly downstream of the cyclone separator which will permit nitric acid concentrations to be measured by the denuder difference technique.

The relative humidity, barometric pressure, orifice pressure, ambient temperature, manifold temperature, meter temperature, and cabinet temperature are measured by the RAAS control unit. The control unit uses a microprocessor to control the various aspects of the system operation. An RS-232 serial port is provided to allow for retrieval of sampling data using a personal computer or other data storage device.

6.4.4 Spiral Ambient Speciation Sampler (SASS™)

This sampler provides five parallel sample cassettes as shown in Figure 6-4. Each cassette has its own spiral size-selective PM_{2.5} inlet, denuder (if applicable), and tandem filter holder. The five cassettes are mounted in an aspirated radiation shield that maintains the sampler temperature close to ambient. Cassette inlets point downward. The sampling head has five independent sampling channels, each operated at a sample flow rate of about 6.0 liters per minute. Ambient air enters each independent sampling inlet and the particle size separated by a

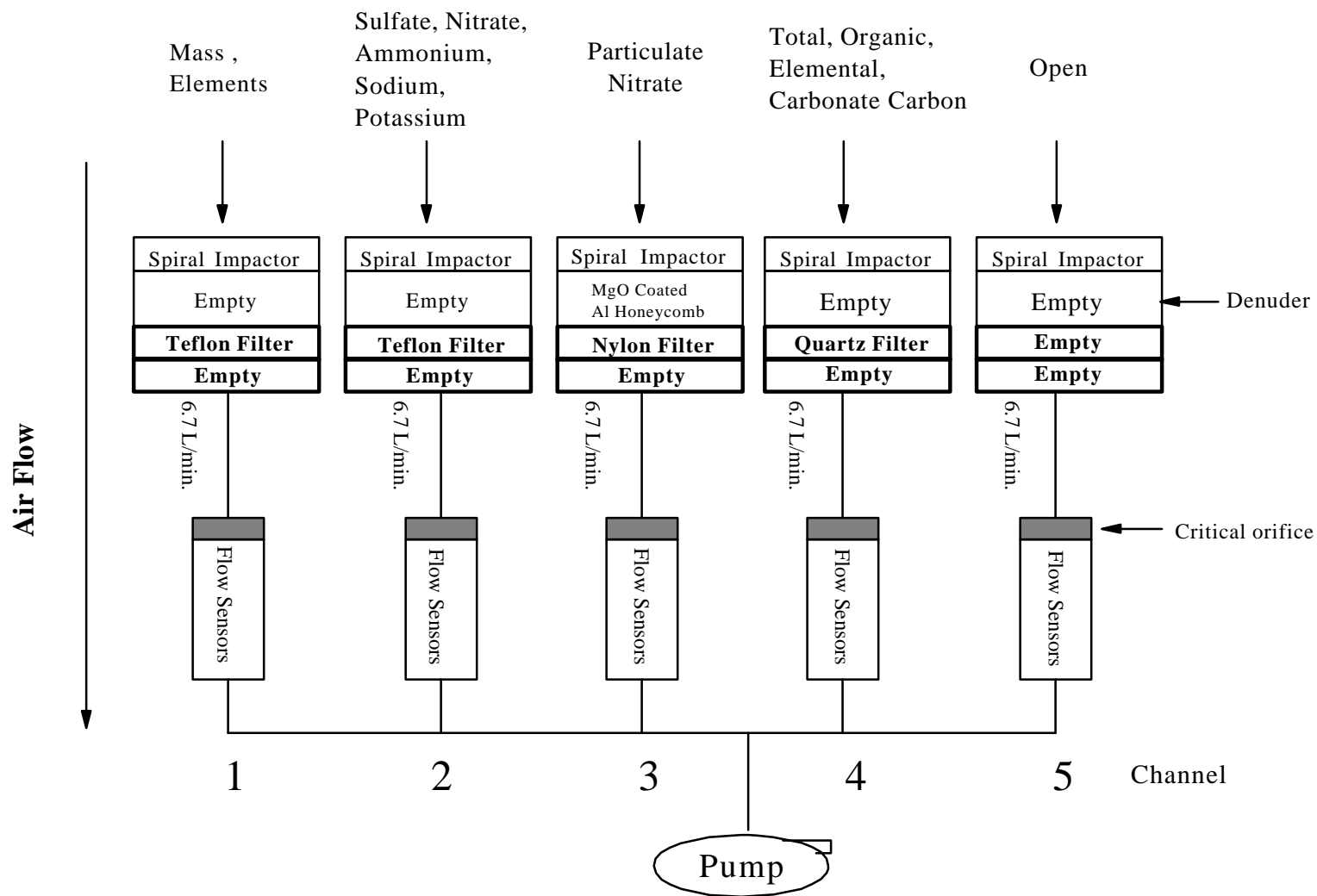


Figure 6-4. Schematic diagram of the SASS™ sampling system configuration.

spiral inlet (John 1997). The particle separator does not require the use of grease or oil anti-bounce agents. The spiral inlet is built into the cassette which allows the inlet to be cleaned in the laboratory before or after each sample event to ensure accurate performance. The sampler does not use a plenum or sample tube which requires field maintenance.

Two types of denuders of multi-cell configuration are provided. The nitric acid denuder is made of aluminum and is coated with magnesium oxide. The carbon denuder, used for collection of semi-volatile species, is made using activated carbon. These denuders remove interfering gases but are not designed to be extracted for direct analysis.

The five cassettes provided with the sampler can be used in multiple configurations. For the routine speciation trends program, the suggested configuration for the five cassettes incorporates:

- ▶ a Teflon® filter for mass and trace elements;
- ▶ MgO-denuder followed by a nylon filter for particulate nitrate;
- ▶ a second Teflon® filter for anions and cations;
- ▶ a quartz filter for carbon; and
- ▶ an additional filter channel of choice for replicate sampling or field blank collection.

Any cassette can be configured with one or two filters or a denuder followed by one or two filters. The filter cassette temperature is monitored and the data logged. The fan aspirated solar radiation shield houses the five individual cassettes and maintains the cassette filter temperature during a sample event to less than 5 °C above ambient temperature. A shielded ambient temperature sensor mounted to the control module logs the ambient temperature.

The flow from each cassette passes through a critical orifice, a mass flow sensor, a valve and then to a common pumping manifold. The critical orifice controls the sample flow rate. The valve located downstream of the filter can be used to close sample lines not in use. The mass flow sensors are used for flow measurement. The flow rate sensors send a signal to the microprocessor which takes the ambient temperature and barometric pressure readings to calculate and display the current volumetric sample rate of each channel. The pumping manifold pressure is read by a mechanical differential pressure gauge leading to a control valve prior to the vacuum pump. The pump uses a rotary carbon vane rated for 20,000 to 30,000 hours of use between vane replacement. The pump is mounted in its own separate enclosure to minimize heat, vibration, isolate power and protect the sampling system from re-entrained dust.

6.5 Other Monitor Types

The monitor types briefly discussed below can also be considered in configuring a non-routine NAMS speciation network. Selection of these monitor types are dependent on the monitoring network and data use objectives.

6.5.1 Single Channel Monitors

Single channel (single inlet assembly and filter medium), FRM samplers are not expected to be routinely used in speciation sampling. A designated FRM or FEM sampler, operated with the appropriate filter media, can be used to collect a sample that may be subsequently analyzed for targeted chemical species. This approach may be used in cases where chemical speciation analyses are performed on a Teflon® filter, after gravimetric analyses has determined a high fine particulate loading. In the case of a Teflon® filter media, the sample can be analyzed for trace elements. The single channel sampler could also be used with other filter media to collect fine particulate for other targeted chemical species. Multiple FRM/FEMs with multiple filter media would be needed to cover the entire group of target chemical species. Alternatively, a uniquely designed sampler could be used to capture fine particulate on nylon and quartz filters, and a FRM sampler used to capture fine particulate on a Teflon® filter.

6.5.2 Continuous Monitors

The EPA encourages the use of continuous monitors as part of the non-routine NAMS speciation monitoring program. Continuous monitors should only be considered for use at routine NAMS as the technology develops and is demonstrated as adequate for use to meet the program and data quality objectives. Continuous monitoring data can be used to provide more timely data reports to the public and collection of data on a more real time basis. Continuous monitors can be used to characterize diurnal patterns of exposure and emissions and are extremely useful in collecting samples during extremely high or low particulate periods.

Currently available continuous monitors for mass include the Tapered Element Oscillating Microbalance (TEOM®), Piezoelectric Microbalance, Beta Attenuation Monitor (BAM), and the Pressure Drop Tape Sampler (CAMMS). Chemical-specific particle monitors include single particle mass spectrometers, a particulate carbon monitor, sulfur analyzer with Flame Photometric Detection (FPD), nitrate analyzers, and elemental analyzers. Precursor gas continuous monitors include a chemiluminescence ammonia analyzer, fluorescence ammonia gas analyzer, and nitric acid analyzers. Refer to the *Guidance for Using Continuous Monitors in PM_{2.5} Monitoring*

Networks (U.S. EPA, 1998b), for additional guidance regarding the use of continuous in-situ measurements of suspended particles, their chemical components, and their gaseous precursors.

6.5.3 Saturation Monitors

EPA encourages State and local air pollution control agencies to conduct short-term, multi-site pollutant monitoring studies using a technique known as saturation monitoring. Saturation monitors are non-reference method, small portable samplers which are readily set-up, operated, and easy to site. Also, because they are relatively inexpensive, it is possible to "saturate" an area with these monitors to assess air quality in areas where high concentrations of pollutants are possible. Saturation monitors are expected to be used to determine "hot spots" of fine particulate. This information can be used to help air pollution control agencies gather preliminary information for speciation sampler siting and evaluate and develop their monitoring networks. Saturation monitoring may also be conducted to characterize the spatial distribution of pollutant concentrations or to evaluate the contributions of sources in support of receptor modeling.

6.5.4 Special Purpose Monitors

A strength in the design of the speciation program is sufficient flexibility to accommodate coordination between the user's needs and advances in sampling technology as they become available. Hence, there is a provision for special purpose monitors (SPMs) as part of the PM_{2.5} program. These monitors can serve a variety of uses including research, regulatory support (i.e., SIPs) and others. The SPMs will not be used as NAMS samplers; they may be collocated with NAMS speciation and FRM samplers. The SPMs may be utilized as part of the speciation program in the sense that subsequent laboratory analysis of the captured particulate may be performed as part of the speciation program, if resources are available.

Special purpose monitors are a separate component of the PM_{2.5} network and as such are not part of the 1,500 network sites. The use of special purpose monitors is expected to complement or be complemented by the use of speciation monitors. Specific requirements of special purpose monitors are not prescribed, so that study designers may tailor monitoring components to the end user needs. Any use of a special purpose monitor should take into consideration the design of the speciation components of the PM fine network and how data can be evaluated.

6.6 Sampling Procedures

Published sampling procedures from several sources are expected to be utilized for compiling the sampling procedures used in the speciation component of the PM_{2.5} program. Sources may include, but are not limited to: sampler manuals, section 2.12 of the QA handbook (U.S. EPA, 1998a), and other sampling methods published from the peer-reviewed literature.

7.0 SAMPLE ANALYSIS

With the goal of ensuring data quality for several thousand filter analyses per year, which will utilize a range of analytical methods for the species required, it is critical to establish an analytical laboratory framework which is consistent to support these needs. One key aspect of the framework is the establishment of standardized SOPs for the routine NAMS speciation analyses. The SOPs will be based on analytical methods with proven application to the analysis of ambient particulate matter filter samples as specified in Table 3-1 of Section 3. In addition to guidance on sampling and handling, the EPA will also develop guidance and documentation for SOPs on the laboratory analysis of the target analytes. The guidance will include laboratory quality assurance guidelines specific to the methods of analysis and guidelines on standardized data reduction, validation, sample handling, chain-of-custody, and reporting formats. The EPA plans for the speciation data to be submitted to the Aerometric Information Retrieval System (AIRS) data base. The EPA is developing laboratory SOPs that are complementary to the techniques used by various agencies and research groups operating ambient air particulate matter speciation programs.

The operational schedule for providing the speciation laboratory support services began with development of a program team of EPA Office of Air Quality Planning and Standards (OAQPS) and Regional Office personnel. The OAQPS has provided the development of the required guidance information and the SOPs with input from the Office of Research and Development (ORD), EPA Regional Offices, and the PM_{2.5} monitoring technical community. Initial deployment of the approximately 50 speciation monitors for the routine trend network is projected for the third quarter of calendar year 1999. Allowing for time by site operators to be trained in the use of the monitors, we project that the laboratory services support portion of the National PM_{2.5} Speciation Program will be in place by July of 1999. The speciation analytical guidelines developed by EPA can also be used by State laboratories with appropriate facilities to provide local support, if appropriate, for an individual State-level monitoring network. In addition EPA is studying the process of evaluating alternative test methodology which may be proposed by States. In such a process, an equivalency methodology guideline would have to be developed that can be used by States to prove that their proposed method performs well as defined by the guidelines.

The methods used for analyses of the filter media include gravimetry (electro-microbalance) for mass and various instrumental methods for determining the chemical composition of the particles. In addition to chemical analyses, special measurement needs may include determining particle size and morphology through optical and/or electron microscopy.

A national laboratory services support program consisting of contracted services with up to three qualified laboratories capable of providing consistent laboratory service support for all of the target analytes will be developed. The extent of the services will depend upon capacity needed, as well as the level of participation by State and local government laboratories for providing analytical services. Analytical support from the contract laboratories will be accessed through three EPA Regional Project Officers or Delivery Order Project Officers (DOPOs).

The contractor shall designate a Services Program Manager (SPM) for work performed under this contract. The SPM shall be responsible for the performance of work issued under this contract in accordance with the terms of the contract. The SPM shall provide information on the status and progress of laboratory services requests to the Project Officer (PO) and Delivery Order Project Officer (DOPO) as needed and submit contract-required reports to the PO/DOPO. The SPM shall notify the PO/DOPO regarding any problems encountered in the performance of work and implement PO/DOPO guidance in the resolution of problems. The SPM shall be responsible for maintaining technical and financial integrity in performance of the requested services, in accordance with EPA-issued delivery orders and contract terms and conditions. A flow diagram of the sample analysis Delivery Order process is given in Figure 7-1.

Analytical needs requests are initially submitted by a state to the corresponding EPA Regional Speciation Coordinator (RSC). The RSC consolidates all analytical requests received from states within their Region and submits them to the appropriate EPA DOPO. The DOPO, in turn, consolidates analytical requests from several regions. The Contracting Officer, as necessary will issue delivery orders to the Contractor's Laboratory. The Contract Laboratory prepares the appropriate filter media for sampling and delivers the media to the appropriate state. After sample collection, the state returns the samples along with sampler information to the Contract Laboratory. In addition, selected field quality assurance samples will be collected by the states and submitted to an appropriate EPA Region QA laboratory for analysis. The Contract Laboratory performs analysis, Level 0 and Level I data validation on all data sets and enters the data into AIRS. After Level I validation and AIRS data entry has been completed, the contractor submits the data sets in both hard copy and electronic format to the appropriate state requesting service. After each data set is submitted to the State, the contractor submits copies of the Level I data validation checklists and hard copies of the monthly analytical data reports to the appropriate EPA DOPO for review, acceptance, and recommendation for payment to the PO.

The most commonly applied aerosol analyses methods can be divided into the following categories: mass, elements, ions, and carbon. It is possible to obtain several different analyses from the same substrate, but not possible to obtain all desired chemical species from a single substrate; therefore, the appropriate filter media, sampling hardware, and analysis methods must

be combined. Depending on the study objectives and sources in an area, different chemical species may need to be added or omitted. A flow diagram of filter processing and analysis activities for the NAMS is shown in Figure 7-2.

The following sections outline the filter analysis methods for the target chemical species categories of elements, ions, and organic carbon.

7.1 Elements

Energy dispersive X-ray fluorescence (EDXRF) by Method Inorganic Compendium of Methods IO-3.3 (U.S. EPA, 1997d) is the method chosen to characterize the elemental composition of the aerosol deposits on PTFE filters for the routine PM_{2.5} NAMS chemical speciation program. Interest in elemental composition is commonly derived from concerns about health effects and the utility of these elements to trace the sources of suspended particles or source characterization. Since sample filters often contain very small amounts of particle deposits, preference is given to methods that can accommodate small sample sizes and require little or no sample preparation or operator time after the samples are placed into the analyzer. X-ray fluorescence (XRF) meets these needs and leaves the sample intact after analysis so it can be submitted for additional examinations by other methods as needed. To obtain the greatest efficiency and sensitivity, XRF typically places the filters in a vacuum which may cause volatile compounds (nitrates and organics) to evaporate. Volatilization will not be an issue for the NAMS sampling systems where the PTFE filters are not subsequently analyzed for volatile species.

In XRF the filter deposit is irradiated by high energy X-rays which causes the ejection of inner shell electrons from the atoms of each element in the sample. When a higher energy electron drops into the vacant lower energy orbital, a fluorescent X-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element. Concentrations are determined by comparing photon counts for a sample with those obtained from thin-film standards of known concentration.

The type of filter is important and thin membrane filters (PTFE) are required so that the background is low and penetration of particles into the matrix of the filter is small. XRF provides rapid, simultaneous, and nondestructive detection of the target elements from Al to Pb. Advantages of using XRF are the quantitative analysis of bulk elemental composition, the ability to perform trace level particulate analysis with sensitivity to ppm levels, and the availability of instrumentation. The XRF method of analysis employs an energy dispersive spectrometer. Analysis atmospheres are selectable with choices of helium or air; helium is used for all target elements except Gd where air is employed because it gives a lower background.

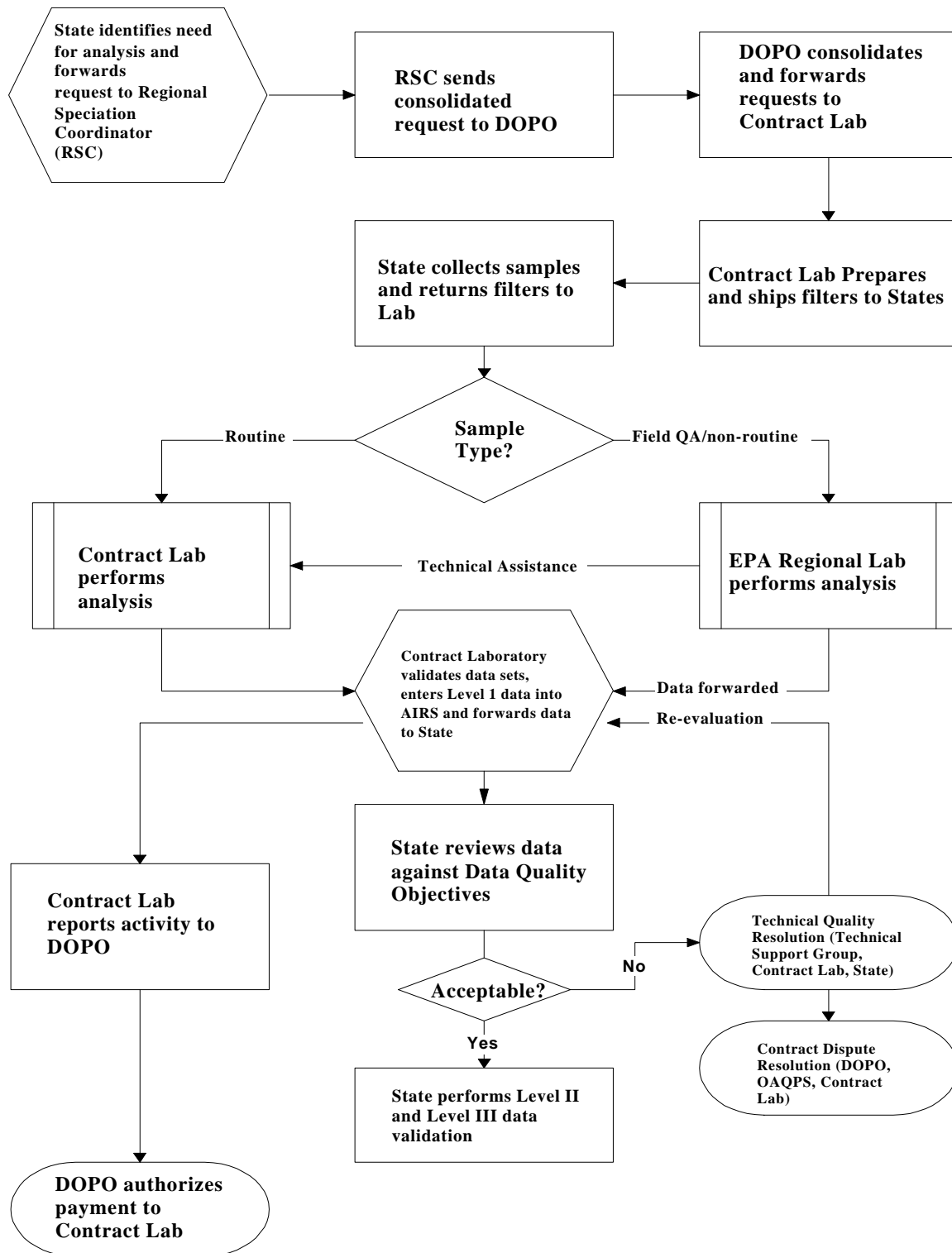


Figure 7-1. Flow diagram of the sample analysis Delivery Order process

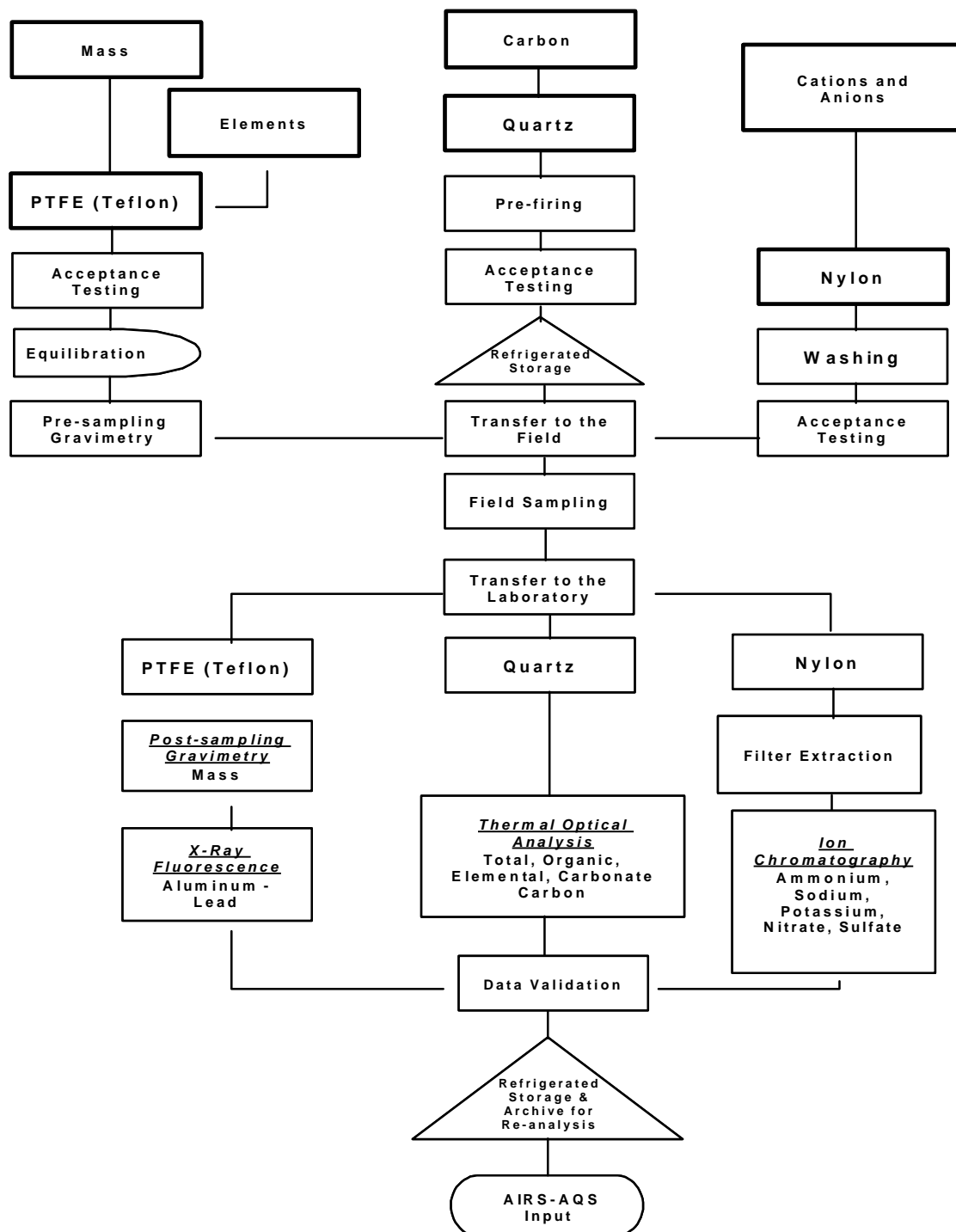


Figure 7-2. Flow diagram of filter processing and analysis activities

Calibration is by far the most complicated task in the operation of the XRF. Recalibration is only performed when a change in fluorescers or x-ray tubes is made or a serious instrument malfunction occurs. Three types of XRF standards are available for calibration: vacuum deposited thin film elements; polymer films; and NIST thin-glass films. The vacuum deposited thin film standards are available for almost all elements analyzed and are used to establish calibration curves. Some standards have high inherent volatility and do not serve well as calibration standards. These are selenium (Se), bromine (Br), mercury (Hg), and elemental arsenic (As). The same set of standards is used every time the spectrometer is calibrated. These standards are sufficiently durable to last many years. Polymer films contain two elements in the form of organo-metallic compounds dissolved in the polymer as described in Dzubay et al., 1988. These standards are available for elements with atomic numbers above 21 (Titanium or heavier). The polymer films and NIST standards are typically used for quality control measures. NIST produces reference materials for iron, lead, potassium, silicon, titanium, and zinc (SRM 1833).

The sensitivity of this method is on the order of few ng/m₃ for 24-hour samples (flow rates of 10-20 liters per minute). This may be a potential issue for the SASS samplers which operate at a flow rate of 6.7 liters per minute for the PTFE filter. Nonetheless, quite often environmental samples have elemental measurements below the detection limit of this method. Thus, analytical uncertainties can have a significant impact on the quality of the data analysis such as for source apportionment studies. It should be mentioned that, during the analysis using XRF, the sample is typically introduced into a chamber that is evacuated and the sample is slightly heated due to the absorption of X-rays or protons. As a result, species that can volatilize such as ammonium nitrate and certain organic compounds can be lost during the analysis. This volatilization is important if the PTFE filter is to be subjected to subsequent analyses of volatile species.

7.2 Ions

Aerosol ions refer to chemical compounds which are soluble in water. The water-soluble portion of suspended particles associates itself with liquid water in the atmosphere when relative humidity increases, thereby changing the light scattering properties of these particles. Different emissions sources may also be distinguished by their soluble and nonsoluble fractions as in the case of soluble potassium. Gaseous precursors can also be converted to their ionic counterparts when they interact with chemicals impregnated on the filter material.

Polyatomic ions such as sulfate, nitrate, and ammonium are quantified by methods such as ion chromatography (IC). Simple ions, such as chloride, and fluoride may also be measured by IC along with the polyatomic ions. When the aerosol deposit is suspected of being acidic, its hydrogen ion content can be determined by a pH electrode or by micro titration. It is important to

keep the filter away from ammonia sources, such as human breath, to minimize neutralization of the acidic compounds.

Applied to aerosol samples, the anions and cations are most commonly analyzed by IC. IC can be used for anions (fluoride, phosphate, chloride, nitrate, sulfate) and cations (potassium, ammonium, sodium) by employing separate columns. All ion analysis methods require a fraction of the filter to be extracted in deionized distilled water and then filtered to remove insoluble residues prior to analysis. The extraction volume should be as small as possible to avoid over-diluting the solution and inhibiting the detection of the desired constituents at levels typical of those found in ambient PM_{2.5} samples. IC is the method used for IMPROVE and chosen for the PM_{2.5} NAMS speciation program for the analysis of the target cations (ammonium, sodium, and potassium) and anions (nitrate and sulfate).

A major sampling requirement for analysis of water-soluble species is that the filter material be hydrophilic, allowing the water to penetrate the filter and fully extract the desired chemical components. A nylon filter is used for volatilized and particulate nitrate and sulfate anions and the ammonium, sodium, and potassium cations. The anions and cations are extracted with ultrapure deionized water. A small amount of ethanol may be used to help wet the nylon filter and improve analyte recovery.

In IC, the sample extract passes through an ion-exchange column which separates the ions for individual quantification, usually by a electroconductivity detector. The anions are separated when passed through a resin consisting of polymer beads coated with quaternary ammonium active sites. The separation is a result of the different affinities of the anions for these sites. After separation and prior to detection, the column effluent and anions enter a suppressor column where the cations are exchanged for H⁺ ions. Species are then detected as their acids by a conductivity meter. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. The IC is especially desirable for particulate samples because it provides results for several ions with a single analysis, low detection limits, and uses a small portion of the filter extract.

The cations are analyzed in the same manner except the sample extract passes through a surface-sulfonated ion exchange resin where separation occurs. After separation and prior to detection, the cations enter a suppressor column where all the anions are exchanged for OH⁻ ions. The species are then detected as their bases (hydroxides) by a conductivity meter. Concentrations of ions and cations are proportional to the conductivity changes.

7.3 Carbonaceous Aerosols

Three classes of carbon are typically measured in ambient aerosol samples collected on pre-fired quartz-fiber filters: 1) organic, volatilized, or non-light absorbing carbon; 2) elemental or light-absorbing carbon; and 3) carbonate carbon. Carbonate-source carbon [i.e., potassium carbonate (K₂CO₃), sodium carbonate (Na₂CO₃), magnesium carbonate (MgCO₃), calcium carbonate (CaCO₃)] may be specifically determined from a second filter section after acidification. Without acidification, the determination of carbonate carbon is not specific and is detected as either organic or elemental carbon.

Two thermal-optical methods currently are in use for the analysis of carbonaceous aerosols. The measurement principle is fundamentally the same, but the methods differ with respect to calibration, analysis time, temperature ramping and settings, types of carbon speciated, and pyrolysis correction technique. The method's pyrolysis correction feature allows correction for the char that forms on the filter during analysis of some materials (e.g., cigarette smoke). Correction for pyrolysis is made by continuously monitoring the filter transmittance (NIOSH Method 5040) or reflectance (TOR) throughout the analysis.

For the NAMS chemical speciation program, total, organic, elemental, and carbonate carbon will be determined by thermal/optical instrumentation specified in NIOSH Method 5040 (NIOSH, 1996, 1998) and described in the literature (Birch and Cary, 1996). Method 5040 was developed for occupational monitoring of diesel particulate, but its evaluation also included a round-robin study involving a variety of carbonaceous aerosols (Birch, 1998). The thermal-optical method is applicable to nonvolatile, carbon-containing species only. Thermal-optical analyzers are practical, economical, and are routinely used for environmental and occupational monitoring of carbonaceous aerosols. Although the number of commercial laboratories currently is limited, an adequate number (3 in the U.S.) are available to cover the analytical demands of this program.

A schematic of the thermal-optical analyzer evaluated by NIOSH researchers is shown in Figure 7-3; an example of the instrument's output, called a 'thermogram,' is given in Figure 7-4. The traces appearing in the thermogram correspond to temperature, filter transmittance, and detector response of the flame ionization detector. Thermal-optical analyzers operate by liberating carbon compounds under different temperature and oxidation environments. A small portion (or punch) is taken from a quartz-fiber filter sample and placed in the sample oven. The oven is purged with helium and the temperature is then stepped to a preset value. Volatilized compounds are converted to carbon dioxide (CO₂) in an oxidizer oven (MnO₂ at 870 °C or higher), the CO₂ is subsequently reduced to methane (CH₄) in a methanator (nickel-impregnated

firebrick heated to ~550 °C in a stream of hydrogen), and CH₄ is quantified by a flame ionization detector (FID). In the second part of the analysis, an oxygen-helium mix is introduced and the remaining carbon is removed through combustion and quantified in the same manner.

In NIOSH Method 5040, the sample oven is purged with helium and the temperature is stepped (to 250, 500, 650 and 850 °C) to volatilize the organic and carbonate-source carbon. It is critical to ensure that trace oxygen is not present during the first part of the analysis. Potential sources of oxygen include leaks and inadequate helium gas purification. If present, trace oxygen will cause organic carbon to be overestimated and elemental carbon correspondingly underestimated. In the second part of the analysis, the temperature is lowered, a 2% oxygen/98% helium mix is introduced, and the temperature is then stepped to a maximum of 940 °C. At the end of the analysis, a calibration gas standard (CH₄) is injected. Correction for pyrolysis is made by continuously monitoring the filter transmittance throughout the analysis. The point at which the filter transmittance returns to its original value is defined as the split between organic and elemental carbon. Designation of the split in this manner allows assignment of pyrolyzed organic carbon to the organic fraction.

In general, thermal-optical methods classify carbon as ‘organic’ or ‘elemental.’ Organic carbon is non-light absorbing carbon that is volatilized in helium as the temperature is stepped to a preset maximum (850 °C). Elemental carbon is light-absorbing carbon and any non-light absorbing carbon evolved after pyrolysis correction. Depending on the sampling environment, carbonates [e.g., potassium carbonate (K₂CO₃), sodium carbonate (Na₂CO₃), magnesium carbonate (MgCO₃), calcium carbonate (CaCO₃)] also may be present in the sample. Carbonate-source carbon is quantified as organic by NIOSH Method 5040, wherein the sample is exposed to 850 °C during the first part of the analysis (i.e., in helium only). Under these conditions, thermal decomposition of carbonate occurs. To quantify carbonate carbon, a second portion of the filter sample is analyzed after its acidification. Carbonate is taken as the difference between the pre- and post-acidification results (Note: the approach assumes a homogeneous filter deposit). Alternatively, carbonate carbon in a simple carbonate (i.e., not a bicarbonate) can be estimated by integrating the carbonate peak (typically the fourth peak in ‘thermogram’). The carbonate peak can be integrated separately within the instrument’s calculation software. This approach normally is taken when higher loadings of carbonate are present. In the case of the TOR method, carbonate in a filter portion is determined through on-line measurement of the carbon dioxide (CO₂) evolved upon acidification. Acid (0.04 M HCl) is injected directly onto the filter portion through an injection port. The sample oven is kept at ambient temperature while CO₂ is evolved, reduced to methane and quantified. (Note: This approach is subject to potential interference of adsorbed CO₂). Typically, carbonate carbon is not speciated in environmental samples because it

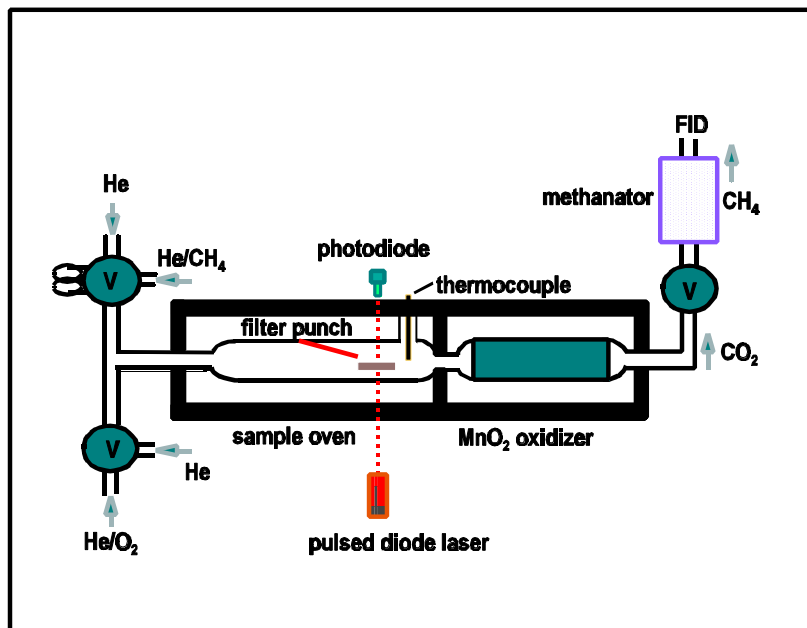


Figure 7-3. Schematic of a Thermal-Optical Analyzer

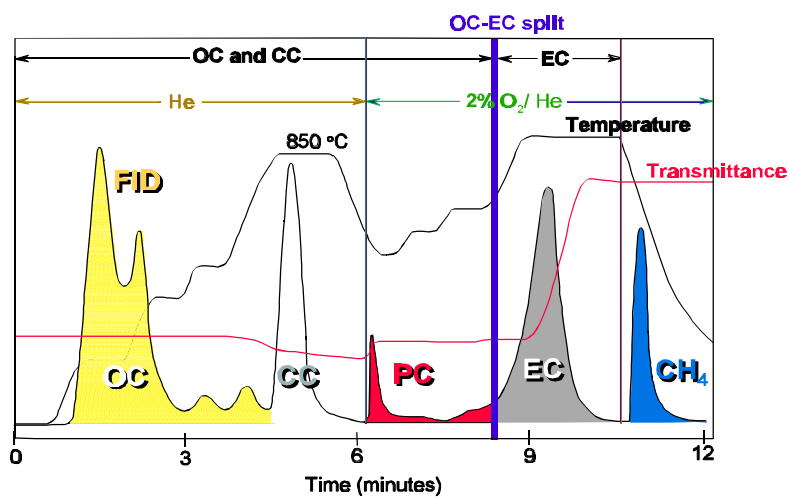


Figure 7-4. Thermogram for a sample containing organic, carbonate, pyrolytic and elemental carbon (OC, CC, PC and EC). The last peak is the methane calibration peak.

has been found to constitute less than 5 percent of the total carbon in most samples (Chow et al., 1993).

It is important to remember that elemental and organic carbon have meaning only in the operational sense. That is, results reflect the method used and the appropriateness of a method depends on its purpose. Operational methods differ from those used for specific, identifiable analytes (e.g., sulfate or sulfur), where a well-defined entity is quantified and laboratory standards are available for its determination. Because elemental and organic carbon are defined operationally, the details of the measurement method must be rigorously prescribed.

Only one organic and one elemental carbon fraction are reported in NIOSH 5040 (total carbon is the sum of these two) and carbonate carbon as simple carbonate (i.e., not a bicarbonate) can be estimated by integrating the carbonate peak (typically the fourth peak in 'thermogram'). In contrast, four types of organic carbon and three types of elemental are defined by the TOR technique. In both instances, different classes of carbon are evolved from the sample during the analysis. In the case of Method 5040, the division into two fractions reflects the purpose of the method (i.e., occupational monitoring of diesel particulate). For other applications (e.g., source apportionment), additional fractions may be appropriate provided that the applied temperature program is repeatable over time. Otherwise, relative information will not be meaningful because non-constant analytical parameters can affect the classification of carbon types.

7.4 Semi-volatile Organic Aerosols

Semi-volatile organic aerosols should not be considered on a routine basis due to the non-routine and research-oriented nature of measuring these species. Identification of the ideal denuder, filter combination, and sorbents and development of routine sampling and analytical methods is complicated due to the number and variety of semi-volatile organic aerosol compounds in the atmosphere and their varying absorptive properties.

The collection of particulate organic matter can be accomplished using particulate sampling instruments equipped with quartz fiber or Teflon®-impregnated glass fiber filters. However, since many organic compounds are distributed between the gas and particle phases, additional sampling techniques are required to measure the particle phase semi-volatile organics. This methodology is susceptible to negative (desorption of semi-volatile compounds from the particles on the filters) and positive (adsorption of gases by the filter material) artifacts. Considerable experimental and theoretical effort has been expended to understand and correct for these vaporization and adsorption effects. Denuder technology has been employed to provide a less artifact-encumbered approach for accurate determination of semi-volatile species because the

gas phase is removed prior to the particulate phase. A sorbent or denuder after the filter may also be employed to collect any semi-volatile material desorbed from the filter.

For quantitation of individual organic compounds the denuder, filter, and sorbent is extracted individually with a suitable organic solvent (or a combination of solvents). The extract is then analyzed by gas chromatography (GC) combined with mass spectrometry (MS) or with other specific detectors. Combined GC/Fourier transform infrared (FTIR)/MS techniques or high performance liquid chromatography (HPLC)/MS techniques are also used.

8.0 QUALITY SYSTEM REQUIREMENTS FOR PM_{2.5} SPECIATION SAMPLING AND ANALYSIS

The quality system is a structured and documented management system describing how and by whom an organization assures quality in its work. The Quality System was established by EPA Order 5360.1 (EPA Order 5360). The order requires all environmental programs conducted by the EPA, or on behalf of the EPA, to be supported by a mandatory Quality System (previously referred to as a Quality Assurance Program). The EPA is responsible for developing the quality system for the PM_{2.5} chemical speciation program. As the standard, EPA has adopted the American National Standard ANSI/ASQC E4-1994, *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs*. When properly designed, a quality system encompasses both quality assurance and quality control through a quality management process by which quality system specifications are planned, implemented, and assessed. To collect data of the right type, quality and quantity to support decisions regarding the chemical speciation component of the National PM_{2.5} Monitoring program, adequate planning and management of a quality system that integrates QA and QC requirements consistent with good field and laboratory practices is necessary.

To communicate the requirements and policies of EPA's Quality System to the Agency's internal organizations, the Quality Assurance Division (QAD) developed the EPA Quality Manual. For the organizations external to EPA (States, Regions, etc.), QAD developed the EPA *Quality System Requirements for Environmental Programs* (EPA QA/R-1). This document and other requirement and guidance documents are available from the EPA QAD homepage at <http://es.epa.gov/ncerqa/qa>. The Quality Manual describes how EPA organizations should implement the policies and requirements of the Quality System as defined in the Order. EPA QA/R-1 should be used to determine general requirements, then external organizations should consult the specific requirements (R-series) documents and guidance (G-series) documents for implementation.

The EPA used the Data Quality Objectives (DQO) process to develop the QA system for the PM_{2.5} program. Meeting the objectives of the PM_{2.5} program requires a combination of QA and QC procedures to evaluate and control measurement uncertainty. As a result, EPA has developed a quality system specifically for PM_{2.5} which incorporates procedures to quantify total measurement uncertainty, as it relates to total precision and total bias. Total bias, precision, and accuracy are defined in 40 CFR Part 58, Appendix A (62 FR 38763). Total bias is defined as systematic or persistent distortion of a measurement process which causes errors in one direction. Total precision is defined as a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions, expressed generally in terms of

standard deviation. Accuracy is defined as the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations. Various QA tools to quantify measurement uncertainty include collocation of monitors at various sites; use of operational flow checks; and implementation of an independent technical systems audit.

The measurement system represents the entire data collection activity. This includes initial filter acceptance testing and equilibration, weighing, and transport; sampling instrument calibration, maintenance and operation; filter handling; laboratory analysis; storage and archival; and finally data analysis and reporting. Detailed QA procedures and guidance for all operational aspects of the PM_{2.5} program using the FRM for mass determinations is detailed in the ***QA Guidance Document 2.12***, (U.S. EPA, 1998a).

A quality system must be developed to permit maximum flexibility yet ensure that the measurement uncertainty is known and under control. To ensure consistency in the application of the Quality System, organizations must implement several components at the organization/program level:

- ▶ Each EPA organization collecting data must prepare a Quality Management Plan (QMP) that details the organization's responsibilities;
- ▶ Data Quality Objectives (DQOs) will be developed to determine the data collection needs and sampling plan;
- ▶ One mandatory component at the project level is the Quality Assurance Project Plan (QAPP);
- ▶ Standard Operating Procedures (SOPs) are developed and documented in the QAPP for use during data collection;
- ▶ Technical System Audits and Reviews; and
- ▶ Following the implementation and planning stages of the program, the Data Quality Assessment (DQA) is performed to determine if the data collected is meeting the intended uses.

The development of data quality objectives and quality assurance project plans support the planning needs of monitoring studies. The implementation phase of a study is carried out using the quality assurance project plan and standard operating procedures. Assessment and redirection, if necessary, of activities within a study are performed by conducting management system reviews, technical assessments and audits, data quality assessment, and data validation.

8.1 Quality Management Plans (QMPs)

A properly developed quality management plan QMP encompasses all QA-related activities, procedures, and responsibilities. The EPA, OAQPS has developed a ***Quality Management Plan*** for intramural and extramural environmental data operations (U.S. EPA, 1996d). There are 10 elements the QMP should contain to ensure consistency. Most of the elements are mandatory, however, some elements may not apply in certain situations. The QMP is the responsibility of senior management within the organization administering the monitoring activities and incorporates the following 10 elements:

- ▶ Management and organization;
- ▶ Quality system description;
- ▶ Personnel qualifications and training;
- ▶ Procurement of items and services;
- ▶ Documentation and records;
- ▶ Computer hardware and software;
- ▶ Planning;
- ▶ Implementation of work processes;
- ▶ Assessment and responses; and
- ▶ Quality improvement.

8.2 Data Quality Objectives (DQOs)

An important concern in the collection and evaluation of ambient air monitoring data is the level of uncertainty of the data. Uncertainty arises due to temporal and spatial variability in the ambient air, variability in the samplers, and variability in the laboratory analyses. The DQO process is a seven-step systematic approach for defining the criteria that the PM_{2.5} speciation data collection design should satisfy, including when to collect samples, where to collect samples, how many samples to collect, and the tolerable level of decision errors. By using the DQO process, EPA will assure that the type, quantity, and quality of the data will be appropriate for the intended application, while guarding against committing resources to data collection efforts that do not support a defensible decision. The outputs of the DQO process are used in developing a sampling design for data collection and preparing the QAPP. In addition, DQO outputs and assumptions are examined and applied during the DQA process.

A PM_{2.5} speciation Work Group of EPA and State participants was convened to complete the DQO process for the PM_{2.5} speciation program. More detailed information on the DQOs and measurement quality objectives is provided in Section 1.2.2 of this document.

8.3 Quality Assurance Project Plans (QAPPs)

The QAPP is a critical planning document for any environmental data operation. The QAPP documents how data operations are planned, implemented, and assessed with respect to the quality of the data required. The purpose of the QAPP is to define how specific QA and QC activities will be performed. The *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations*, EPA QA/R-5 and *EPA Guidance for Quality Assurance Project Plans*, EPA QA/G-5 are documents that should be consulted in the preparation of the QAPP. The QAPP is composed of 25 elements grouped into four classes: 1) project management; 2) measurement and data acquisition ; 3) assessment and oversight; and 4) data validation and usability. Not all elements are addressed for every project; however, other projects may require additional elements not contained in the original 25. The final decision on the elements to be included in the QAPP is made by the overseeing EPA organization. **QAPPs are required for all environmental data operations that acquire, generate, or compile data and are performed by or on behalf of the EPA. A QAPP must be in place prior to the start of data collection.**

A stand-alone QAPP will be developed by the EPA for the PM_{2.5} chemical speciation trends network. QA issues for filter preparation, sample handling and transport for mass measurements will be comparable to those stated in the of the *QA Guidance Document 2.12* (U.S. EPA, 1998a). Place holders will be included for sampler specific SOPs to be incorporated based on the sampler type chosen. With exception of the sampler specific SOPs, the QAPP will be equally applicable to the entire chemical speciation program. Prior to data collection, a QAPP is required to be prepared by each organization implementing a non-trends NAMS network.

During the planning phase, DQO outputs are documented int the QAPP in the form of measurement performance criteria and QA/QC procedures. SOPs are also included or referenced in the QAPP. Development of the QAPP provides a transition from planning to implementation. During implementation, data are collected in accordance with the QAPP. During the assessment phase, data are verified and validated according to procedures and criteria specified in the QAPP, and DQA analyzes the data to determine if the assumptions and criteria documented in the QAPP were met.

The QAPP is a planning document for environment data collection operations that describe the necessary quality assurance (QA) and quality control (QC). Quality assurance is an integrated system of management activities to ensure that a process or service is of the type and quality needed and expected by the end user (e.g., State or local regulatory agencies, EPA, general public, etc.). Quality control is defined as the overall system of technical activities that compares performance against defined standards to verify that stated requirements are met.

Every measurement consists of measurement quality objectives that refer to values of precision, accuracy, and validity. Quality control and quality auditing establish the precision, accuracy, and validity of measured values. Quality assurance integrates quality control, quality auditing, measurement method validation, and sample validation into the measurement process. The results of quality assurance are data values with specified precision, accuracy, and validity. Quality auditing is performed by personnel who are independent of those performing the procedures. A separate quality assurance officer performs these audits.

Quality control is the responsibility of each operator and is intended to prevent, identify, correct, and define the consequences of difficulties which might affect the precision and accuracy, and or validity of the measurements. The QC activities include: modifying standard operating procedures (SOPs) to be followed during sampling, chemical analysis, and data processing; equipment overhaul, repair, acceptance testing, and spare parts; operator training, supervision, and support; periodic calibrations and performance tests, which include blank and replicate analyses; and quality auditing.

8.4 Standard Operating Procedures (SOPs)

SOPs document the specific procedures necessary to carry out routine or repetitive technical or administrative activities. SOPs are specific to the organization or facility where they will be used and ensure that the procedure is conducted in a standardized and reliable manner. SOPs provide standardization and consistency of methods and protocols used to ensure data comparability, credibility, defensibility and quality. The SOPs codify the actions which are taken to implement a measurement process over a specified time period. State-of-the-art scientific information is incorporated into the SOP with each revision.

SOPs are developed at the organizational level and applied at the project level. SOPs provide input to the QAPP, used for implementation of the data collection activities, and used as a specification during technical systems audits. SOPs are an important part of the personnel training program and must be kept current to be effective. For PM_{2.5} chemical speciation sampling and analysis, SOPs are needed which effectively detail major field sampling and laboratory operations. Guidance for the preparation of SOPs is given in EPA QA/G-6, *Guidance for the Preparation of Standard Operating Procedures*. Each SOP should include the following basic elements:

- ▶ A brief summary of the measurement method, its principles of operation, scope and applicability, expected accuracy and precision, and the assumptions which must be met for it to be valid.

- ▶ A list of materials, equipment, reagents, and suppliers. Specifications are given for each expendable item.
- ▶ Definition of terms (acronyms, abbreviations).
- ▶ Health and safety warnings indicating operations that could result in personal injury or loss of life and an explanation of what will happen if the procedure is not followed.
- ▶ Cautions indicating activities that could result in equipment damage, degradation of samples or possible invalidation of results.
- ▶ Personnel qualifications and designation of the individual to be responsible for each part of the procedure.
- ▶ A general traceability path, the designation of primary standards or reference materials, tolerances for transfer standards, and a schedule for transfer standard verification.
- ▶ Start-up, routine, and shut-down operating procedures and an abbreviated checklist.
- ▶ Copies of data forms with examples of filled-out forms.
- ▶ Routine maintenance schedules, maintenance procedures, and troubleshooting tips.
- ▶ Internal calibration and performance testing procedures and schedules.
- ▶ External performance auditing schedules.
- ▶ References to relevant literature and related standard operating procedures.
- ▶ Data and records management.

The *Quality Assurance Guidance Document 2.12* (U.S. EPA, 1998a), *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Part 1* (U.S. EPA, 1998g), and the *Model QAPP for the PM_{2.5} Ambient Air Monitoring Program at State and Local Air Monitoring Stations*, EPA-454/R-98-005, has been issued by the EPA to address PM_{2.5} mass monitoring with designated FRMs. Table 8-1 gives an example of the SOPs that may be required for PM_{2.5} chemical speciation. SOPs should be reviewed and updated annually to ensure that procedures specified in the SOPs are actually being followed in field and laboratory operations.

8.5 Technical Systems Audits and Performance Evaluations

The quality auditing function consists of technical systems audits and performance evaluations. Technical systems audits include an on-site review and inspection of a State or local agency's monitoring program to assess compliance with established regulations that govern the collection, analysis, validation and reporting of the air quality data. Technical systems audits of the agencies operating the SLAMS chemical speciation program shall be conducted at least every 3 years by the EPA Regional QA laboratories. Detailed information regarding the performance of technical system audits is found in *Quality Assurance Handbook for Air Pollution Measurement Systems* (U.S. EPA, 1998g). A systems audit should consist of three phases: 1)

pre-audit activities; 2) on-site audit activities; and 3) post-audit activities. Systems audits start with the preparation of an audit plan which documents items such as the audit scope, purpose, criteria, activities, and time line. A review of the operational and QC procedures are performed to assess whether they are adequate to ensure that data meet the specified levels of accuracy and precision. After reviewing the procedures, the auditor examines all phases of the measurement or data processing activity to determine that the procedures are being followed and the operational staff are properly trained. The findings of the audit are documented in a technical systems audit report. The systems audit is intended to be a cooperative assessment resulting in improved data rather than a judgmental activity.

Performance Evaluations (PEs) are a means of independently verifying and evaluating the quality of data from a measurement process, or overall measurement system. Performance audits establish whether the predetermined specifications are being achieved in practice. The performance audit challenges the measurement/analysis system with known standards traceable to a primary standard. These samples can be used to control and evaluate bias, accuracy, and precision and to determine whether the measurement quality objectives and DQOs are satisfied. Performance evaluation samples can also be used to determine inter- and intra-laboratory variability and temporal variability. For data processing, the performance audit consists of independently processing sections of the data and comparing the results. Performance objectives should be specified for the field or laboratory instruments on which performance audits are conducted. Audit findings are compared against these values to decide whether or not remedial action is needed.

An example of field and laboratory performance audit observations is given in Table 8-2. Performance audits for field operation will be addressed in the EPA's Quality Assurance Project Plan for NAMS trend sites, therefore only laboratory performance audits are discussed here. The quality audit function is incorporated into the chemical speciation monitoring network to ensure the accuracy, precision, and validity of mass and chemical speciation measurements.

The laboratory performance audit consists of the submission of known standards to routine laboratory procedures and of an interlaboratory comparison of those standards. Gravimetric analysis can be audited by weighing independent Class M or NIST-traceable standard weights and Teflon®-membrane filters, which will be pre-weighed and post-weighed at the primary laboratory and the audit laboratory for comparison. To audit the analysis of soluble species on quartz-fiber filters, a solution containing sulfate, sodium, nitrate, ammonium, and potassium is prepared and deposited in known amounts on quartz-fiber filters. Samples at a minimum of three concentrations are submitted to the routine chemical analyses for nitrate, ammonium, potassium, and sulfate by ion chromatography. To audit the analysis of the elements

by x-ray fluorescence (XRF) on Teflon®-membrane filters, several thin film micromatter pure-element deposits are submitted for routine XRF analysis.

Table 8-1
Examples of Standard Operating Procedures

Subject	Observation/Method	Standard Operating Procedure
Chain-of-Custody	Filter Pack/Cassette Handling	Assembling, Disassembling, and Cleaning Procedures
	Shipping and Receiving	Sample Shipping, Receiving, and Chain-of-Custody
	Nylon Filter Cleaning	Preparation of Nylon Filters for Nitric Acid or Total Nitrate Sampling
	Quartz Filter Pre-Firing	Pre-firing of Quartz Fiber Filters for Carbonaceous Material Sampling
Chemical Analysis	Sample Sectioning	Sectioning of Teflon® and Quartz Filter Samples
	Filter Extraction	Extraction of Ionic Species from Filter Samples
	Mass	Gravimetric Analysis Procedures
	Elements (Al to Pb)	X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples
	Nitrate (NO₃⁻) Sulfate (SO₄²⁻)	Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography
	Ammonium (NH₄⁺)	Analysis of Filter Extracts for Ammonium by ion chromatography
	Soluble Sodium (Na⁺) Soluble Potassium (K⁺)	Analysis of Filter Extracts by ion chromatography
	Total Organic Carbon (OC) Total Elemental Carbon (EC) Total Carbon (TC)	Thermal Optical Carbon Analysis of Aerosol Filter Samples
Aerosol Data	Data Validation	Field, Mass, and Chemical Data Processing and Data Validation

At the present time there are no widely accepted standards for elemental and organic carbon. Potassium acid phthalate solutions can be deposited on quartz-fiber filters to create organic carbon standards. A minimum of three sets of analyses at each concentration level and three blank filters should be analyzed for each audited chemical species.

8.6 Data Quality Assessment (DQA)

A DQA is the scientific and statistical evaluation of the data obtained to determine if those data are of the right type, quality, and quantity to support the intended use. The DQA is broad reaching and encompasses an evaluation of all aspects of the program from DQOs through data reporting. A very important aspect of the DQA is that it provides a measure of the quality of data which is important for data analyses and data use. The five steps of the DQA process are shown in Figure 8.1. Although the steps of the DQA are presented in a linear sequence, the process is iterative in nature. The DQA is designed to promote an understanding of how well the data satisfy their intended uses. The DQA approach parallels the activities typical of analyzing a data set for the first time. The five step procedure is not intended to be a definitive analysis of a

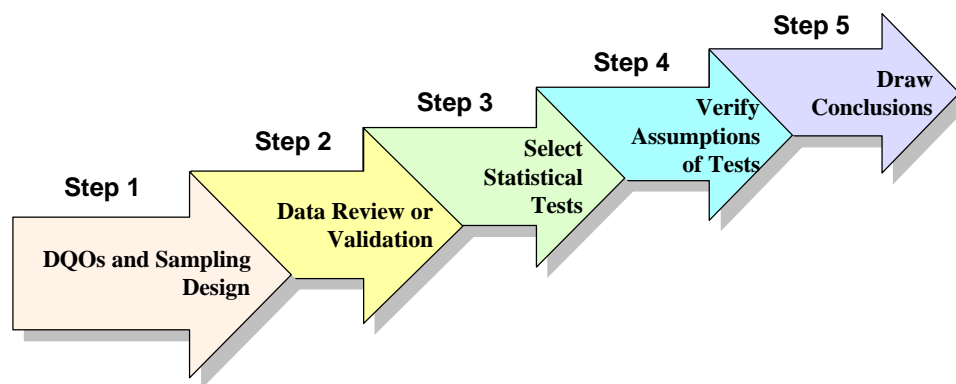


Figure 8-1. Five steps of the Data Quality Assessment

project or problem, but instead to provide an initial assessment on the “reasonableness” of the data that have been generated. The QA guidance available in EPA QA/G-9, *Guidance for Data Quality Assessment*, is directed towards the analysis of relatively small data sets containing data that have been collected in a relatively simple fashion.

The DQA process is built on a fundamental premise that data quality as a concept is meaningful only as it relates to the intended use of the data. One must know in what context the data set will be used in order to establish a relevant yardstick for judging whether the data set is adequate. The steps of the DQA are described in more detail below.

1. **Review of the Data Quality Objectives (DQOs) and Sampling Design:** The DQOs are reviewed to assure that they are still applicable. If DQOs have not been developed, as may be the case for SPMs or non-routine NAMS monitors, specify DQOs before evaluating the data. Review the sampling design and data collection documentation for consistency with the DQOs.
2. **Preliminary Data Review:** Review QA reports, calculate basic statistics, and generate graphs of the data. Use this information to learn about the structure of the data and identify patterns or potential anomalies. In addition to the review of the QA reports by the State and regional data analysts, OAQPS/EMAD will prepare a report showing the quality of the data as the data begin to be reported. The purpose of the report is to summarize the quality of the data and to identify potential QA concerns. For example, certain speciation monitors may show more variability than others or certain seasons may show more variability. Such information is necessary for evaluating the data and providing direction for improvements in the PM_{2.5} speciation network.
3. **Determination of Appropriate Statistical Test:** Select the most appropriate statistics for summarizing and analyzing the data based on review of the DQOs, the sampling design, and the preliminary data review. Identify key underlying assumptions about the data that must hold true for the statistical procedures to be valid.
4. **Verification of the Assumptions of the Statistical Test:** Evaluate whether the underlying data assumptions hold, or whether departures are acceptable, given the actual data and other information about the study.
5. **Conclusions Drawn from the Data:** Perform statistical tests and document the inferences drawn from those tests and evaluate performance of the sampling design.

The DQA process will be conducted by the EPA and reveal whether the decisions for which the data were collected can be made with the desired confidence, given the quality and quantity of the monitored data. If the data provide evidence strongly in favor of one conclusion, then the decision maker can proceed knowing that the decision will be supported by unambiguous data. However, if the data do not provide strong evidence, then the decision maker has the information needed to determine whether to proceed with the decision, despite the reduced level of confidence, or whether to collect more or different data with the goal of increasing the confidence level. The strength of the DQA process is in the design which promotes an understanding of how well the data satisfy their intended use by progressing in a logical and efficient manner.

The DQA needs to be conducted at the spatial resolution of a State or smaller geographical area. The reason for this is that the overriding objective of the speciation network will vary spatially, as may the quality of the monitored data. An exception to this is the network of 50 NAMS sites deployed with the primary objective of monitoring national trends in the constituents of PM_{2.5}. For these 50 sites, the objective is the same and SOPs need development to minimize the variability in the quality of the collected data.

8.7 Regional Laboratory QA

Four EPA and Regional labs will comprise the Laboratory QA support group. This group is responsible for providing routine QA support to the chemical speciation program, which includes conducting QA sample analyses, analyses for special studies, and technical QA support to the contract laboratories, States and EPA. The link of the Regional QA labs to the overall contract laboratories and the filter analysis and data processing is discussed in Section 7.0. Each EPA region is responsible for resolving Contractor laboratory QA issues, analysis of QA samples (field duplicates, round robin samples, audit samples), performing technical systems audits, and providing technical support for QA. QA support for field duplicates, colocated samples, and special studies will be provided for all routine speciation target analytes using the same methods as those used by the contract laboratories.

Table 8-2
Examples of Laboratory Performance Evaluation Procedures

Parameter	Measurement Device	Performance Test Frequency	Performance Standard	Calibration Frequency	Calibration Standard	Audit Frequency	Audit Standard	Primary Standard
Aerosol Sample Flow	Candidate Chemical Speciation Sampler	Once per day	Calibrated Rotameter	At the Beginning and End of one-month Sampling Period or When Performance Tests are Out of Specification	Calibrated Rotameter	Once every 2 months	Mass Flow Meter	Certified Roots Meter
PM _{2.5}	Electromicro-balance	1/10 Samples 3/10 Samples	NBS Class M Standard Weights Replicate	At Beginning of Weighing Session	NBS Class M Standard Weights	Once every 2 months	NBS Class M Standard Weights	NBS Class M Standard Weights
PM _{2.5}	XRF Analyzer	1/15 Samples 1/15 Samples	NBS Thin Film Standards Replicate	Quarterly	Micromatter Thin Film Standards	Once every 2 months	Prepared Standard Deposit	Thin Film Standard
PM _{2.5} anions and cations	Chromatographic Analyzer	1/10 Samples 1/10 Samples	Solution Standards Replicate	At Beginning of Each Run	ACS Certified Standard Solutions	Once every 2 months	N/A	ACS Certified Chemicals
PM _{2.5} Carbon	Thermal/Optical Carbon Analyzer	1/10 Samples 1/10 Samples	Methane Gas Replicate	Once/2-months or When Performance Test Tolerances Not Met	Methane, CO ₂ , Gas and ACS Certified KHP	Once every 2 months	Standard KHP Solutions	ACS Certified Chemicals

9.0 DATA VALIDATION AND DATA MANAGEMENT

This section provides a general discussion of the general specifications relative to data validation, data base requirements, substrate data processing and AIRS. EPA plans to develop specific data validation guidance for use by States, Regions, and laboratories implementing the NAMS speciation program. This guidance is slated for completion by the third quarter of 1999.

9.1 Data Validation

Data validation is the most important part of the overall data generation and processing system. The data must be reviewed and validated to assure the overall quality of the measurement prior to inclusion into the Aerometric Information Retrieval System -Air Quality Subsystem (AIRS-AQS) data base. Data validation is used in conjunction with the program objectives, DQOs, and program QA/QC to remove inconsistencies in the data set and to improve data quality. Data validation consists of systematic procedures developed to identify deviations from measurement assumptions and procedures. Timely data validation is required to more easily resolve data issues and unusual events and take the necessary corrective actions to minimize the generation of additional data that may be invalid or suspect. Four levels or categories generally apply to validation of monitoring data:

- Level I) Routine checks made during the initial data processing and generation of data, including proper data file identification, review of unusual events, review of field data sheets and result reports, instrument performance checks and deterministic relationships.
- Level II) Tests for internal consistency to identify values in the data which appear atypical when compared to values of the entire or whole data set.
- Level III) Comparison of the current data set with historical data to verify consistency over time. This level can be considered a part of the data interpretation or analysis process.
- Level IV) Tests for parallel consistency with data sets from the same population (region, period of time, air mass, etc.) to identify systematic bias. This level can also be considered a part of the data interpretation or analysis process.

Level I validation establishes the traceability of the integrated data set and takes place mainly in the field and in the laboratory. Level I validation consists of flagging samples when significant deviations from measurement assumptions have occurred. Computer file entries are verified against data sheets; values are eliminated for measurements which are known to be invalid

because of instrument malfunctions; and measurement values are adjusted due to quantifiable calibration or interference biases.

Level II validation takes place after data from various measurement methods have been assembled in the master data base or LIMS (Laboratory Information Management System). Level II applies internal consistency tests based on known physical relationships between variables of the assembled data. Several internal consistency checks can be applied to evaluate validity when different particle size fractions are measured and submitted to chemical analyses. These include comparisons between collocated measurements; comparisons between mass concentrations and the weighted sum of chemical species; checks for physical and chemical consistency; and charge balances between anions and cations. As discovered, data adjustments for quantifiable biases can be made in Level II validation..

Level III validation is part of the descriptive data analysis or data interpretation process. Level III validation can include time series analysis, correlation matrices, material balance, quantitative statistical analyses, and modeling. The first assumption upon finding a measurement inconsistent with physical expectations is that the unusual value is due to a measurement error. After tracing the path of the measurement, if nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. Unusual values are identified during the data interpretation process as extreme values or outliers.

Level IV validation is typically performed as part of data interpretation and consists of tests for consistency with data sets from the same population. Level IV validation is done after the data is placed in the AIRS-AQS data base and can include the same interpretive analyses discussed in Level III validation. Data sets from the same region, air mass, or period of time are analyzed for consistency.

Given that there are separate field sampling, laboratory analysis, QA and data analysis components of the speciation program, various pieces of each level of validation will logically fall under each of these areas. No one area will contain the responsibility for an entire level of data validation. For example, components of Level I data validation will be done independently but not be duplicated by both the field and lab personnel. The State data analyst of laboratory personnel may perform certain components of Level II and Level III validation.

9.2 Data Base Requirements and AIRS

Substrate data processing is a very important part of the overall data management process. Data base requirements exist for the managing and processing data at the field and laboratory

level, prior to submitting the data to the AIRS-AQS data base. Aerosol data processing consists of six general tasks:

1. **Record Keeping** - All relevant information obtained at the time an operation is performed is registered on field data sheets, the data logger, or other transfer medium.
2. **Input** - The data are transferred from the recording medium into computer-accessible files or an electronic data base.
3. **Merging** - Data from various files pertaining to an individual sample or sampling day are retrieved and related to each other.
4. **Calculations** - Data items are combined in mathematical expressions to yield a desired concentration result. These include the pollutant concentration, which must be reported in $\mu\text{g}/\text{m}^3$, accuracy, and precision.
5. **Data Validation** - Data are validated according to the Level I through IV data validation steps as described above.
6. **Output** - Data are arranged into the desired format for input to the AIRS-AQS and subsequently formatted for data interpretation and modeling software.

Aerosol data processing requires the assignment of identification (ID) codes to filter substrates. Field data records should include a recording of the IDs and their corresponding sampling sites, sampling dates, sampling times, sampling duration, sample flow rates, and deviations from normal sampling procedures. Laboratory records should contain instrument recordings of analytical outputs. Data validation is performed and should provide for formatting and reporting of concentrations in $\mu\text{g}/\text{m}^3$ and all data validation activities.

Field data can be entered into computerized data forms. Substrate IDs can be bar-coded and then entered with a scanner rather than being typed. The screen forms have limits that do not allow entry of values lying outside a certain range. Every data item entered is verified against the original data sheet by the data processing supervisor. A data base structure, which contains fields for chemical concentrations and a level of uncertainty is formed. Each record should contain sample IDs, sample volumes, sample times, sampling sites, and sampling dates, which are integrated into this structure from the field records. All other fields contain the missing data default value. These defaults are replaced by the result data as they become available. In this way, it is possible to determine which analyses have been completed and which have not.

The laboratory chain-of-custody is used to track the disposition of each sample and can be consulted to determine the fate of missing values in the master data base. This independent tracking is needed to prevent sample IDs from being mixed up or samples being lost.

Laboratories having the capacity to analyze a high volume of samples, usually employ a LIMS to acquire, record, manipulate, store, and archive their data. Not all automated laboratory systems are LIMS. Automated laboratory systems that record data but do not allow changes to the data are not LIMS. For example, an instrument that measures weights and produces or maintains a read-out of the weight is not a LIMS, if the true reading cannot be adjusted if needed prior to recording. If data entered into automated laboratory systems can be manipulated or changed in any way by the action of a person prior to being recorded, then that automated laboratory system is a LIMS. The EPA has developed guidance on Good Automated Laboratory Practices (GALP), *Good Automated Laboratory Practices* (U.S. EPA, 1995b), which addresses principles for ensuring data integrity in automated laboratory operations. In summary, the following areas are addressed:

Laboratory Management - Following the collection, analysis, and processing of LIMS data, laboratory management shall ensure the overall quality of the data provided. Laboratory management ensures that personnel understand their roles; the QA unit monitors LIMS activities; resources are adequate and available; corrective action is promptly taken; and SOPs are approved.

Personnel - Personnel must have adequate education, training, and experience to perform assigned LIMS functions; and have a current summary of their training, experience, and job description, including their knowledge relevant to LIMS design and operation, maintained at the facility.

Quality Assurance Unit – The QA unit inspect the LIMS at intervals adequate to ensure the integrity of the LIMS Raw Data.

LIMS Raw Data - Procedures and practices to verify the accuracy of LIMS raw data are documented and included in the laboratory SOPs, and managed.

Software - SOPs are established, approved, and managed for the software used to collect, analyze, process or maintain the LIMS raw data.

Security - Laboratory management shall ensure security practices to assure the integrity of LIMS data are adequate. EPA laboratories and those of its agents (contractors) shall comply with EPA's information security policy.

Hardware - LIMS hardware shall be of adequate design and capacity, and a description of the hardware documented and maintained. The hardware shall be installed and operated in accordance with the manufacturer's recommendations and be adequately tested, inspected, and maintained.

Comprehensive Testing - When LIMS raw data are collected, analyzed, processed, or maintained, laboratory management shall ensure that comprehensive testing of LIMS performance is conducted, at least once every 24 months or more frequently as a result of software or hardware changes/modifications. These tests shall be documented, and the documentation shall be retained and available for auditing when appropriate.

Record Retention - The retention of LIMS raw data, documentation, and records pertaining to the LIMS will comply with EPA contract, statute, or regulation; and SOPs for retention are documented, maintained, and managed.

Facilities - The environmental conditions of the facility housing the data are regulated to protect against data loss, and the facility has adequate environmental storage capability for retention of raw data, storage media, documentation, and records.

Standard Operating Procedures - Each SOP should be readily available and current. SOPs are periodically reviewed at a frequency adequate to ensure that they describe the current procedures. A historical file of SOPs shall be maintained.

After data for a record have been assembled, data validation comparisons should be conducted as discussed in Section 9.1. A data validation summary is maintained and associated with each record to provide traceability for data adjustments, replacements, or deletions. Field and laboratory data validation flags are assigned as part of the data validation process. Data validation summaries accompany the final data base. This data base must be converted to AIRS-AQS format for subsequent submission to the AIRS-AQS. All PM_{2.5} chemical speciation data must be entered into AIRS. The EPA, OAQPS, Information Transfer and Program Integration Division (ITPID) administers the AIRS-AQS. The AQS contains data submitted by States, local and reporting organizations. The AIRS-AQS includes descriptions of air monitoring sites, monitoring equipment, measured concentrations of pollutants and related parameters.

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